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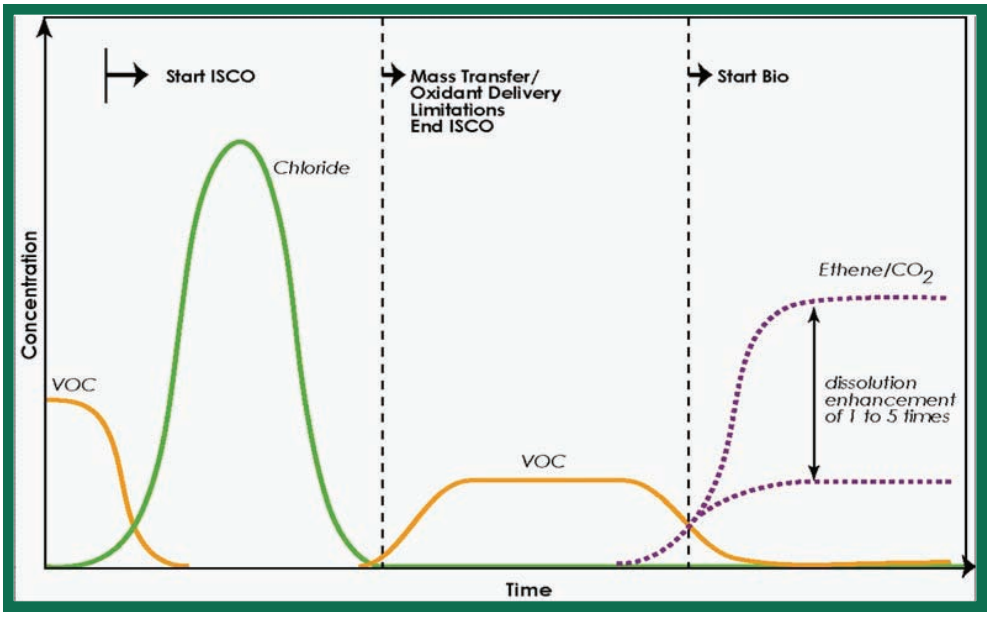

Remediation of DNAPL Through Sequential In Situ Chemical Oxidation and Bioaugmentation

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LIST OF ACRONYMS AND ABBREVIATIONS

bgs	below ground surface
C-C	carbon-carbon
CCAFB	Cape Canaveral Air Force Base
CO_2	carbon dioxide
cis-DCE	*cis*-1,2 dichloroethene
DGGE	denaturing gradient gel electrophoresis
Dhc	*Dehalococcoides*
DHG	dissolved hydrocarbon gas (or gases)
DNAPL	dense non-aqueous phase liquid
DoD	Department of Defense
DOE	Department of Energy
DOT	Department of Transportation
ESB	Engineering Support Building
ESTCP	Environmental Security Technology Certification Program
EVO	emulsified vegetable oil
EZVI	emulsified zero-valent iron
Geosyntec	Geosyntec Consultants, Incorporated
ISB	enhanced in situ bioremediation
ISCO	in situ chemical oxidation
ITRC	Interstate Technology and Regulatory Council
KSC	Kennedy Space Center
LC-34	Launch Complex 34
LSU	lower sand unit
MCL	maximum contaminant level
MFGU	middle fine grained unit
MNA	monitored natural attenuation
MnO_2	manganese dioxide
MnO_4^-	permanganate
MSDS	material safety data sheet
NAPL	non-aqueous phase liquid
NASA	National Aeronautics and Space Administration

LIST OF ACRONYMS AND ABBREVIATIONS

O&M	operations and maintenance
ORP	oxidation reduction potential
OSHA	Occupational Safety and Health Administration
PCE	tetrachloroethene
PCR	polymerase chain reaction
PLFA	phospholipid fatty acid
PID	photoionization detector
ppb	parts per billion
ppmv	parts per million by volume
PTA	pilot test area
QPCR	quantitative polymerase chain reaction
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
SERDP	Strategic Environmental Research and Development Program
SPH	six-phase heating
TCE	trichloroethene
USEPA	U.S. Environmental Protection Agency
USU	upper sand unit
UT	University of Toronto
VC	vinyl chloride
VFA	volatile fatty acids
VOC	volatile organic compound

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1.0 EXECUTIVE SUMMARY

The principal benefit of in situ chemical oxidation (ISCO) using permanganate is that it aggressively enhances dissolution and destruction of the target contaminants within a relatively short period of time (i.e., months to years). But the economic benefits of this technology diminish as the mass of target chemicals decreases. To date, the most effective applications of ISCO have been to rapidly destroy the readily accessible target chemical mass within the source area. However, ISCO potentially can be coupled with a less costly mass removal technology such as in situ bioremediation (ISB), thereby reducing the overall remediation costs.

The main objectives of this project were to assess the technical feasibility of sequential application of these technologies (ISCO and ISB) to evaluate the effects of this combined treatment on overall cost and performance, and to identify the optimal timing of the transition from ISCO to ISB. Technical problems limited the ability to meet these objectives fully—biofouling caused significant downtime during operations and operations were severely impacted by a series of hurricanes. As a result the demonstration was terminated earlier than planned. Nevertheless, the project has yielded valuable findings, including:

- Electron donor addition (biostimulation) after ISCO resulted in partial biodegradation of trichloroethene (TCE) to cis-dichloroethene, although bioaugmentation was needed for complete biodegradation (to low levels of ethene).
- Over the duration of the pilot test, ISB did not significantly increase the mass flux of chloroethenes after ISCO.
- The precipitated manganese dioxide (MnO_2) produced by permanganate reduction, which can oxidize some organic compounds, did not abiotically degrade any of the chloroethenes or ethene.
- MnO_2 greatly increases the electron donor demand above that typically required to reduced the dissolved constituents (e.g., oxygen, nitrate, sulfate, and the target chloroethenes) during ISB.
- MnO_2 can be dissolved by the activity of Mn(IV)-reducing bacteria, that appear to preferentially utilize hydrogen and thus inhibit the activity of dechlorinating bacteria such as *Dehalococcoides* (*Dhc*), which use hydrogen as their sole electron donor.
- The limited cost assessment indicated there was a significant cost and schedule advantage for the sequential treatment strategy when compared to pump and treat, or the use of ISCO alone (assuming a reasonable mass flux enhancement can be achieved during ISB).

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2.0 INTRODUCTION

2.1 BACKGROUND

Chlorinated solvents such as tetrachloroethene (PCE) and TCE are present in groundwater as dense non-aqueous phase liquids (DNAPL) at many U.S. Department of Defense (DoD), Department of Energy (DOE), and related contractor facilities. DNAPLs have low aqueous solubilities, but even these values may exceed regulatory criteria by as much as five orders of magnitude (Pankow and Cherry, 1996). As a result, these compounds only slowly dissolve in groundwater and act as long-term sources of groundwater contamination.

The physico-chemical properties of PCE and TCE make these contaminants particularly difficult to remove from groundwater systems. It is now widely recognized that removal using groundwater extraction and above-ground treatment (pump-and-treat) is only effective as a containment approach due to the slow dissolution of solvents from residual or pooled DNAPL sources (U.S. Environmental Protection Agency [USEPA], 1992; National Research Council, 1994). These systems will require operation over indefinite periods of time (i.e., decades to centuries) incurring continuing annual operations and maintenance (O&M) costs over that period. Accordingly, treatment technologies that enhance the dissolution rate of a DNAPL will decrease the remediation time, which ultimately reduces total life-cycle costs of remediation. The difficulty in removing PCE and TCE DNAPL from contaminated aquifers has emphasized the need for effective in situ treatment technologies that target DNAPL source zones. In situ treatment technologies capable of treating DNAPL source zones are listed in Table 1. Those technologies offering mass destruction are advantageous in that the DNAPL mass is not simply transferred into a second matrix but destroyed in situ.

Table 1. Summary of DNAPL remediation technologies.

Focus	Technology Class	Remediation Technology	Physico-Chemical Remediation Process
Plume Management	Reactive barriers	Zero-valent iron	- Minimizes the migration of contaminated groundwater by intercepting and degrading the dissolved phase contaminants
	Containment	Impermeable walls Pump-and-Treat	- Minimizes the migration of contaminated groundwater by either preventing groundwater flow or hydraulically containing the contaminated groundwater
	Bioremediation	Monitored natural attenuation	- minimizes migration of contaminated groundwater by degrading the dissolved phase contaminant
Source Management	Flushing	Alcohol surfactant oxidant	- Removes DNAPL by either mobilizing pure phase or increasing the solubility of the contaminant - Removes DNAPL by rapidly degrading the dissolved phase contaminant
	Volatilization	Soil vapor extraction air sparging In-well stripping	- Removes vapor phase contaminant from either the vadose or saturated zones by enhancing partitioning into the vapor phase
	Thermal	Steam flushing electrical heating In situ vitrification	- Removes DNAPL by enhancing volatilization and/or mobilizing the pure phase
	Enhanced bioremediation	Biostimulation	- Removes DNAPL mass by enhancing the rate of biodegradation within the source zone
		Bioaugmentation	- Minimizes migration of contaminated groundwater (increases degradation rate and promotes complete dechlorination to ethene) by increasing the activity of dechlorinating microorganisms

Laboratory experimentation and field applications have demonstrated that ISCO with permanganate (MnO_4^-) is an effective technique for degrading chlorinated solvents (e.g., Schnarr et al., 1998; Hood and Thomson, 2000; Thomson et al., 2000). ISCO typically involves injection and/or recirculation of a concentrated oxidant solution to promote rapid oxidation of the target chemicals. Permanganate attacks the carbon-carbon (C-C) double bonds in chlorinated ethenes (e.g., TCE), mineralizing the target compound to inorganic products such as carbon dioxide (CO_2), water, and chloride (Cl^-).

The principal benefit of the ISCO technology is that it aggressively enhances dissolution and destruction of the target contaminants within a relatively short period of time (i.e., months to years) in comparison to conventional treatment technologies. However, the cost-benefit of ISCO diminishes as the mass of target chemicals decreases, particularly at sites where low permeability zones limit mass transfer. Results of a technology status review of in situ oxidation technology demonstrations indicated that rebound of volatile organic compound (VOC) concentrations was observed at many ISCO sites, and that re-application of the oxidant or implementation of a secondary polishing technology was required (Environmental Security Technology Certification Program [ESTCP], 1999). Based on the current status of the technology, it appears that the most effective application of ISCO consists of rapid destruction of the readily accessible target chemical mass within the source area coupled with a less costly and more passive in situ remediation approach to control the remaining mass (e.g., ISB or natural attenuation).

Like ISCO, in situ bioremediation technologies have rapidly evolved in recent years to the point where demonstrations are being conducted to evaluate the technical and economic feasibility of DNAPL source zone bioremediation. Like ISCO, rapid biological destruction of dissolved-phase chlorinated solvents can enhance dissolution of the chlorinated solvent DNAPLs, to reduce the duration and cost of remediation. However, while TCE half-lives are on the order of minutes with ISCO, biodegradation rates are typically on the order of hours to days, suggesting that the rate of DNAPL removal using ISB is likely to be less than that achieved during ISCO, but may still be high enough so that ISB can be used as a secondary source treatment technology. This is contingent upon increasing microbial activity in the vicinity of the DNAPL and overcoming mass transfer limitations. In the event that mass transfer enhancements by ISB are negligible, the enhanced biodegradation rates provide significant benefit through biological containment of the remaining VOCs in groundwater.

Unfortunately, little is known regarding the impact of ISCO on groundwater geochemistry and microbiology. Specifically, the application of an aggressive oxidant such as permanganate may have adverse impacts on the indigenous microbial community such that bioremediation of the chlorinated solvents cannot be stimulated through electron donor addition alone. Reseeding (bioaugmentation) of the ISCO treatment area with microorganisms capable of degrading chlorinated solvents (e.g., dehalorespirers) may be required to permit successful implementation of in situ bioremediation as a polishing technology. To achieve this objective, several dehalogenating microbial cultures are available for field application, including the Pinellas (Ellis et al., 2000; Harkness et al., 1999) and KB-1™ (Duhamel et al., 2002; Major et al., 2002) cultures. Both cultures contain *Dhc* bacteria, which are the only dehalorespiring bacteria capable of completely dechlorinating TCE to ethene (Maymo-Gatell et al., 1997), and have been used in

laboratory and/or field trials to successfully promote rapid and complete dechlorination of PCE and TCE to ethene.

Coupling the ISCO primary source treatment technology, to rapidly remove accessible DNAPL mass, with semi-passive in situ bioremediation via biostimulation (if possible) or bioaugmentation (likely to be required) as a secondary source treatment or plume containment technology is an attractive remediation approach. The combined treatment approach is expected to reduce the duration and cost of remediation at chlorinated solvent sites (relative to application of either technology alone or in conjunction with other technologies), which will in turn reduce the financial drain of these sites on DoD funds and programs.

2.2 OBJECTIVES OF THE DEMONSTRATION

The primary objectives of the demonstration were to:

- Determine the impacts of ISCO application on the natural microbial community (biomass, diversity), specifically on the presence of dehalorespiring bacteria, and determine whether the post-ISCO indigenous microbial community can be stimulated to biodegrade remaining chlorinated solvents, or whether bioaugmentation is required to reseed the treatment area to promote in situ bioremediation
- Assess the impacts of ISCO on the groundwater chemistry and microbiology and identify aquifer conditioning requirements for application of in situ bioremediation
- Identify the appropriate switchover point from chemical oxidation to enhanced bioremediation
- Demonstrate in situ bioremediation of VOCs remaining in groundwater following ISCO treatment using either biostimulation (addition of electron donors only) or bioaugmentation (addition of dehalorespiring bacteria and electron donors), as required
- Evaluate whether ISB will act as a secondary mass removal technology or mass containment technology following ISCO.

The study approach consisted of a field trial to demonstrate that biostimulation and/or bioaugmentation can stimulate complete dechlorination of a nontoxic product (i.e., providing a mass containment) and whether the mass flux from a source zone increases when biological dehalorespiration activity is enhanced through nutrient addition and bioaugmentation (i.e., providing a secondary source removal technology post-ISCO). The field demonstration was conducted at Launch Complex 34 (LC-34), an unused launch facility at the Kennedy Space Center (KSC) in Florida, where an extensive TCE DNAPL source is present in groundwater in the area adjacent to the Engineering Support Building (ESB). The results of this technology demonstration were incorporated into the process for selecting a final source zone remediation technology. The pilot test area (PTA) for this technology demonstration was selected to be within the ISCO test plot, which was used for a previous demonstration of ISCO using

permanganate, which is further described in Section 3. The selection of LC-34 as the demonstration site reduced the requirement for ISCO as part of this technology demonstration.

During the demonstration, groundwater was recirculated through the PTA at a constant groundwater velocity. A number of treatment phases were used to evaluate the rate of DNAPL removal and the extent of VOC treatment. Each phase was operated for sufficient duration to establish a near steady-state rate of TCE removal under each of the different operating conditions (i.e., baseline groundwater recirculation only, electron donor addition, electron donor addition plus bioaugmentation). The demonstration provided important data that enhances the understanding of the sequential technology for in situ remediation.

2.3 REGULATORY DRIVERS

Since 1976, both PCE and TCE have been designated by USEPA as priority pollutants. The Safe Drinking Water Act Amendments of 1986 strictly regulate these compounds; each has a maximum contaminant level (MCL) in drinking water of 5 parts per billion (ppb) (USEPA, 1996).

Additionally, the DoD lists the following directives as high priority requirements:

- Navy: 1.I.1.g. *Improved remediation of groundwater contaminated with chlorinated hydrocarbons and other organics*
- Army: A(1.2.c) *Enhanced Alternative and In-Situ Treatment Technologies for Solvents and Halogenated Organics in Groundwater (96-97)*
- Air Force: 2008: *Methods and Remedial Techniques Are Needed to More Effectively Treat Groundwater Contaminated with Chlorinated Solvents Such as TCE, TCA, and PCE.*

3.0 TECHNOLOGY

The following sections provide an overview of the theoretical impacts of ISCO on ISB and an overview of previous studies evaluating the sequential ISCO/ISB approach (Section 3.2); and a description of the advantages and disadvantages of the technology (Section 3.3).

3.1 TECHNOLOGY DESCRIPTION

3.1.1 Technology Development and Application

Conventional groundwater remediation technologies have emphasized treatment of contaminants present in the dissolved phase plume migrating downgradient of the DNAPL source area. While a number of plume management technologies, including pump-and-treat, air sparging, and permeable reactive barriers, have proven effective in containing plume migration, the low solute flux from many DNAPL source zones implies that O&M of plume remediation technologies will be required for an indefinite duration ranging from decades to centuries (Johnson and Pankow, 1992). Research in the last decade has emphasized the development of treatment technologies, such as those described in Table 1, which aggressively remove and/or degrade DNAPL. These technologies provide the benefit of reducing the time required for cleanup by increasing the mass flux from the source zone; however, the applicability of these technologies may be limited by cost, regulatory acceptance, and uncertain performance.

The performance of remediation technologies can be expressed in terms of the enhancement in the rate of DNAPL removal during treatment relative to the rate of removal under conditions of ambient groundwater flow (i.e., no applied treatment). Bioremediation, generally thought to be of limited effectiveness in DNAPL source areas (Pankow and Cherry, 1996), results in a lower mass transfer enhancement than ISCO but requires only the addition of a dilute nutrient solution (i.e., minimal operating cost) while ISCO, which can result in a relatively large mass transfer enhancement, requires the addition of concentrated permanganate solution (i.e., high operating cost). Strategically coupling these technologies to match the rate of DNAPL mass removal from the source may be used to minimize the lifetime cost of source area remediation.

Figure 1 presents a scenario where the primary mass removal technology (i.e., ISCO), which is capable of rapid removal rates, efficiently removes DNAPL mass until the point of diminishing returns occurs; however, as the rate of mass removal decreases, the cost of per unit DNAPL mass removed will rapidly increase. Accordingly, a secondary, lower operating cost mass removal technology (i.e., ISB) with a lower maximum mass removal rate capability, is better suited to the mass transfer conditions at this time.

Although ISCO involves the comparatively high operating cost of continuous oxidant addition, this technology can result in up to 40-fold enhancements of the DNAPL removal rate (Schnarr et al., 1998). In contrast, the operating cost of ISB is much lower (requiring the addition of relatively inexpensive electron donors) while a maximum of 16-fold enhancements in the rate of DNAPL removal may be achievable (Cope and Hughes, 2001). As previously discussed, DNAPL removal using ISB is contingent on mass transfer rate limitations imposed by the deposition of MnO_2, and in the event that there is no rate enhancement, this technology may be used to simply contain the remaining VOCs in groundwater.

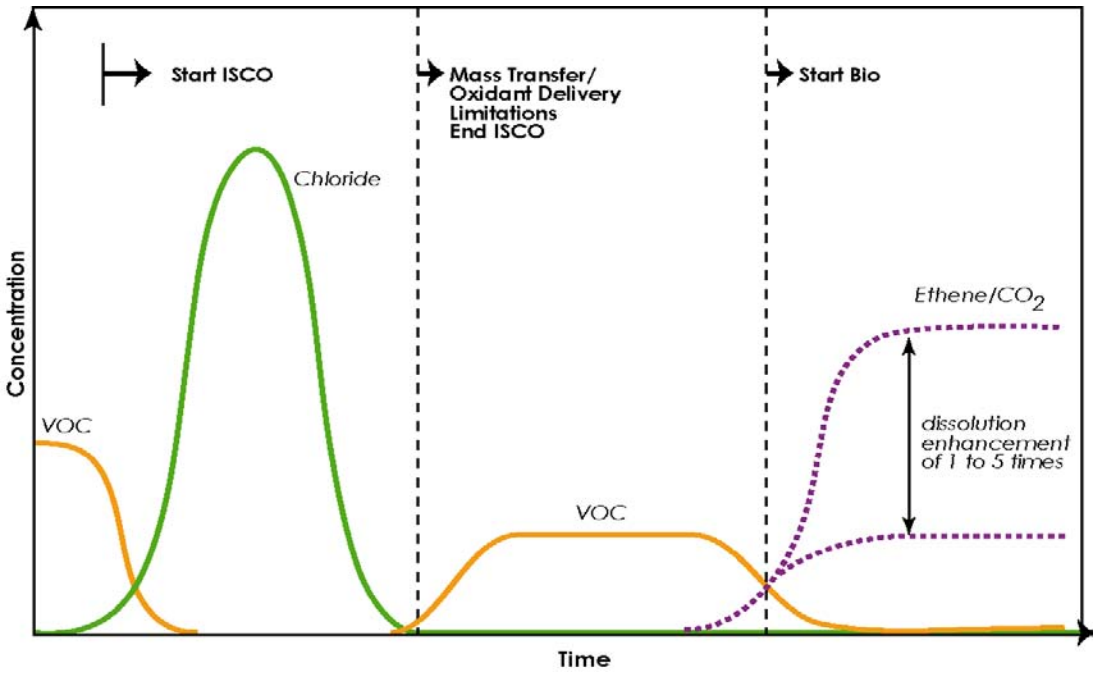

Figure 1. Conceptual model of contaminant mass removal during sequential ISCO and ISB.

3.1.2 Switching from In Situ Chemical Oxidation to Enhanced In Situ Bioremediation

After the initial phase of ISCO, in which the rate of DNAPL removal is very high, the rate typically decreases to the point that it does not increase the rate of DNAPL removal over that expected by flushing the source area with groundwater only. Accordingly, applying a lower cost remediation technology is appropriate. The switchover point may be determined based on either the total rate of DNAPL removal (as determined by either measurement of concentrations of the parent compound or chloride, an oxidation reaction product) or by comparison to the background chloride concentration. Under conditions where the minimum criteria for the effectiveness of ISCO are not achieved (i.e., no measurable mass transfer enhancement) a complementary remediation technology with a lower operating cost may be more appropriately applied.

3.1.3 Potential Impacts of ISCO on Enhanced In Situ Bioremediation

Adding permanganate to groundwater can potentially result in both direct and indirect impacts on the subsequent use of ISB. Residual permanganate in the target treatment zone may directly impact ISB by inhibiting reductive dechlorination and reacting with the electron donor. Through disinfection, ISCO will reduce the microbial numbers. If the remaining biomass is not sufficient to support reductive dechlorination processes, longer periods of electron donor addition will be required. However, removal of the indigenous biomass may enhance subsequent bioaugmentation of the treatment zone by decreasing the competition for electron donors.

In addition to directly impacting the biomass present in the treatment zone and reacting with electron donors, the deposition of manganese oxides (e.g., MnO_2, the dominant form of reduced manganese) in the treatment zone may have indirect impacts on the performance of enhanced

bioremediation processes following ISCO. This may potentially include pH increases, oxidation of electron donors, or inhibition of reductive dechlorination processes.

3.2 PREVIOUS TESTING OF THE TECHNOLOGY

To date, a limited number of laboratory investigations have evaluated the impacts of ISCO using permanganate on microbial populations and dechlorinating activity; these include:

- Reductions in indigenous populations of aerobic and anaerobic heterotrophs, nitrate, nitrite, and sulfate reducers, and methanogens following permanganate treatment ranged from 47% to 99.95% (Klens et al., 2001). Results from six months after treatment suggest that the population of heterotrophic aerobic microorganisms rebounded although anaerobic heterotrophic microorganisms had minimal regrowth.
- At least one microcosm study of sequential ISCO and bioremediation (Rowland et al., 2001) suggests that ISCO does not intrinsically inhibit the dechlorinating activity of the microbial population.
- Azadpour-Keeley et al. (2004) reported on microbial sampling conducted to evaluate the effects of ISCO testing at LC-34 in Cape Canaveral, FL, and showed that biomass had increased markedly from pre-ISCO levels at one month post-ISCO, but then returned to pre-ISCO levels over the remainder of the monitoring period.
- Macbeth et al. (2005) used microbial community profiling and quantitative polymerase chain reaction (QPCR) testing to track *Dhc*-like species prior to and one year following MnO_4^- injection. Decreases in both biomass and diversity were observed, but these partially recovered one year after residual MnO_4^- concentrations had decreased. *Dhc* was found to be present at low levels in the treatment area post-ISCO.

In summary, there are a number of laboratory and field studies that suggest that application of ISCO may have no long-term impacts upon a follow-on ISB application. However, while these studies have shown that biomass returns post-ISCO, they have not clearly demonstrated a return of microbial activity resulting in dechlorination of chlorinated VOCs.

3.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The main advantages of the technology are:

- Enhancing the dissolution rate of a DNAPL will decrease clean-up times.
- Mass will be destroyed and not simply transferred to another medium.
- Expansion of a treatment area to include uncertainties related to the exact DNAPL distribution are unlikely to be difficult or significantly increase total cost.
- The enhanced bioremediation process provides a long-term, lower cost, polishing of VOCs remaining after ISCO.

- Lower expected capital and O&M costs than alternative technologies (see the ESTCP project ER-0116 Final Report, Table 2-1).

The main limitations of the technology are:

- The need to understand and identify the source extent and mass to minimize the volume of the zone requiring treatment (i.e., minimize cost)
- Inaccessible DNAPL mass
- The cost of the amendments required (i.e., MnO_4^-, electron donor)
- Weak advective-dispersive solute transport processes which may limit the delivery of treatment reagents (e.g., MnO_4^-, electron donors) to the DNAPL
- The occurrence of geochemical conditions (e.g., high sulfate) that may be inhibitory to biodegradation
- The presence of co-contaminants that may be inhibitory to biodegradation (e.g., chloroform, hydrogen sulfide).

In addition, there is the potential that ISCO will adversely impact the subsequent implementation of ISB. Adverse impacts could occur: (1) during ISCO through disinfection of the treatment zone and/or (2) as a result of long-term changes in the groundwater geochemistry.

4.0 PERFORMANCE OBJECTIVES

The performance objectives that were used to meet the project objectives and to evaluate the performance and cost of the demonstration are provided in Table 2.

Table 2. Performance objectives.

Type of Performance Objective	Primary Performance Criteria	Data Requirement	Success Criteria
Qualitative	Activity of microbial community	Microbial analysis, microcosm studies using PTA samples, changes in VOC concentrations	Microbial activity present prior to the addition of nutrients and/or bioaugmentation; community activity increased after these additions
	Increase extent of dehalogenation	VOC analysis at monitoring wells, extraction wells, and multilevel wells	Complete dehalogenation to ethene
	VOC concentration reduction	VOC analysis at monitoring wells, extraction wells, and multilevel wells	Some VOC concentration reduced in areas of high microbial activity
Quantitative	Increase in microbial biomass	Microbial analysis, microcosm studies using PTA samples	Increase in microbial biomass above the base case treatment[1]
	Increased mass flux from DNAPL during treatment > after amendment with electron donor > after bioaugmentation	VOC analysis at monitoring wells, extraction wells, and multilevel wells	Increase in mass flux above the base case treatment[1]
	Reduce DNAPL mass	VOC analysis in soil cores at baseline and comparison to VOC concentration measurements over demonstration	Reduction in DNAPL present at start of base case treatment[1]

Notes:
[1]Base case treatment – operation of pilot system post-oxidation without addition of electron donor/nutrients or bioaugmentation

Successful implementation of the technology would demonstrate that the technology results in significant post-ISCO microbial activity, a statistically significant increase in the degradation rate of aqueous TCE with rapid and complete degradation to ethene. As a consequence of the microbial activity and VOC degradation, the rate of TCE DNAPL removal would increase as compared to pump-and-treat, decreasing the duration of remediation required for complete restoration of the PTA.

It was intended that the demonstration would continue longer to fully evaluate the technology; however, system operation was severely impacted by a series of hurricanes and ultimately the demonstration was terminated. Despite this early termination, the data gathered was sufficient to evaluate the performance objectives of the demonstration, as described in Section 7.

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5.0 SITE DESCRIPTION

5.1 SITE LOCATION

The location of LC-34 is provided in Figure 2. Due to the relatively simple geology at the site and the known presence of DNAPL, a number of research-oriented technology demonstrations have been conducted at LC-34, including performance evaluations of ISCO using potassium permanganate, six-phase heating (SPH), steam (Battelle, 2001a), bioaugmentation (Battelle, 2004b) and emulsified zero-valent iron (EZVI) (Battelle, 2004a). The locations of these demonstrations and the estimated extent of their influence are presented in Figure 3.

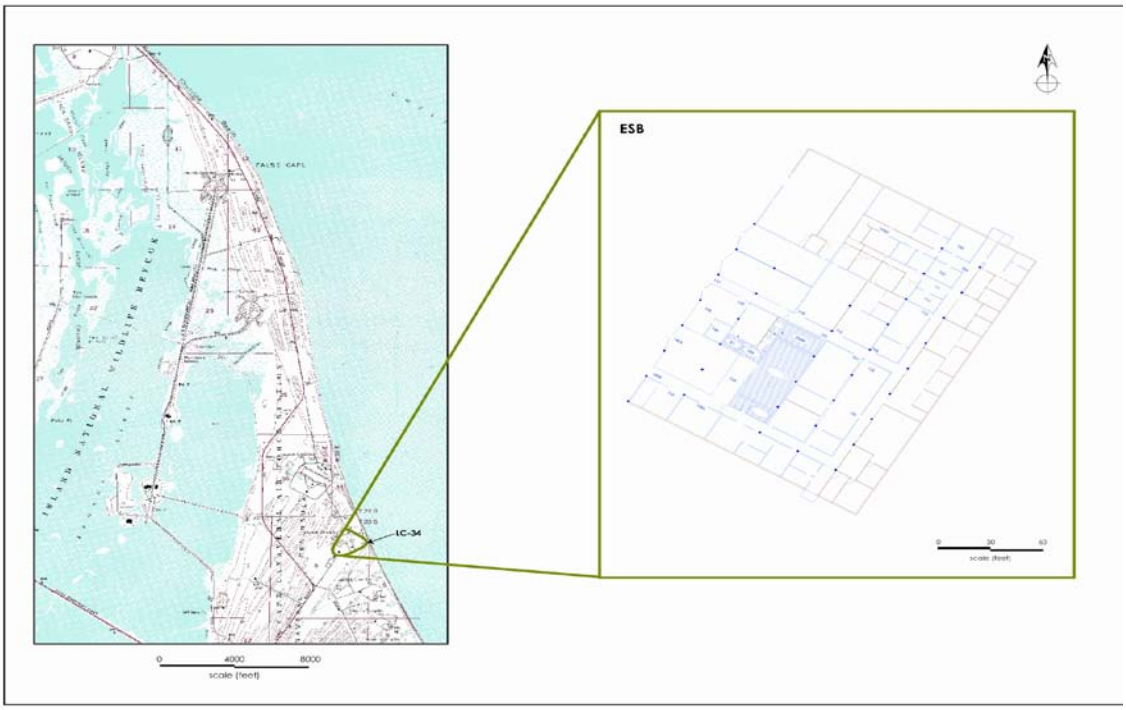

Figure 2. Location of Cape Canaveral Air Force Base, Cape Canaveral, FL.

In 1999, a demonstration of ISCO using permanganate at LC-34 was completed in a 75 ft x 50 ft test plot adjacent to ESB. During the demonstration, 842,985 gallons of a potassium permanganate solution (typical concentration of 1.4% to 2%) was injected into the ISCO test plot through a drive-point injection system. The total mass of MnO_4^- used during the demonstration was 68,479 kilograms (kg).

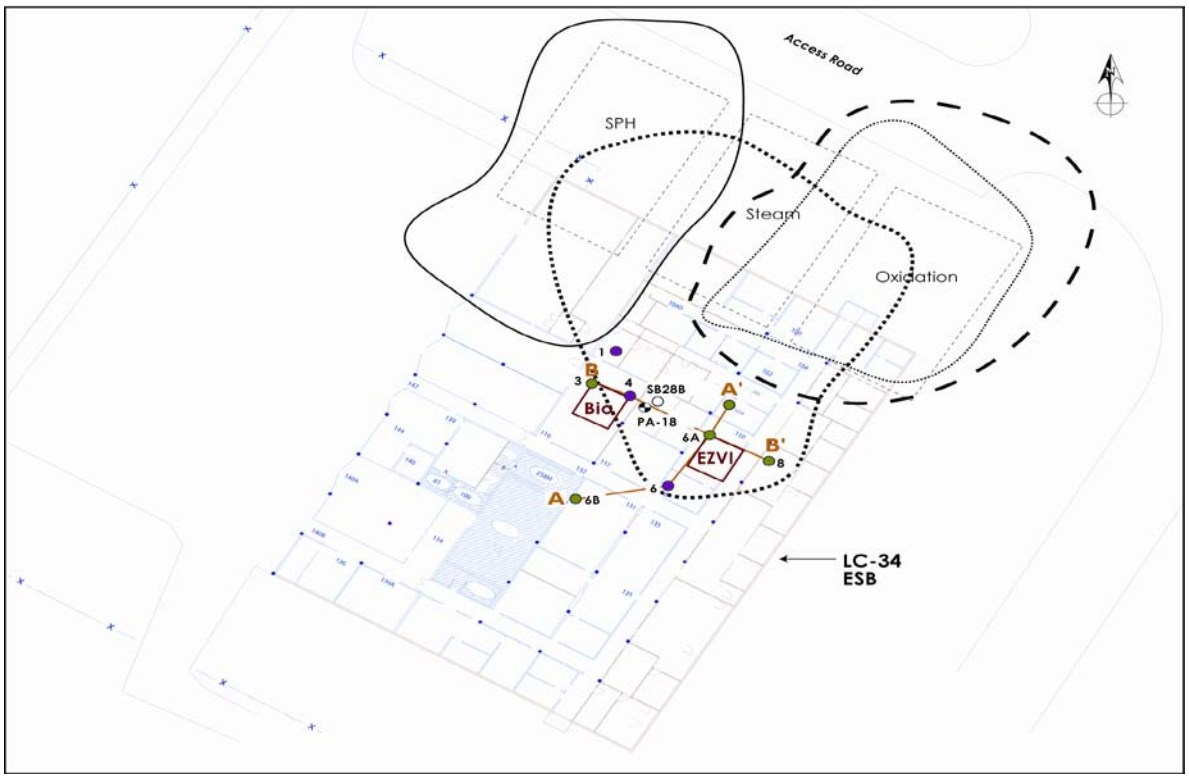

Figure 3. Site plan and technology demonstration locations at LC-34.

5.2 SITE GEOLOGY AND HYDROGEOLOGY

Hydrogeological conditions at LC-34 are highly favorable to the implementation of a recirculation-based remediation technology. The aquifer consists of relatively homogeneous sand and silty sands and is easily instrumented using low-cost, direct-push drilling technologies (i.e., GeoProbe). A surficial aquifer and a semiconfined aquifer beneath a clay unit comprise the major water bearing units at LC-34. The surficial aquifer extends from the water table to approximately 45 ft below ground surface (bgs). The clay confining unit ranges in thickness from 1 to 3 ft. The surficial aquifer is subdivided into the upper sand unit (USU), the middle fine-grained unit (MFGU), and the lower sand unit (LSU) (Eddy-Dilek et al., 1998). The USU is composed of medium- to coarse-grained sand and crushed shells and extends from ground surface to approximately 18 to 25 ft bgs. The MFGU, which varies in thickness from about 4 to 14 ft, is composed of gray, fine-grained silty/clayey sand and generally contains finer-grained sediment than the remainder of the aquifer unit. The MFGU is thicker to the north of the ESB and appears to thin towards the south and west of the ESB. The LSU, the deepest subunit of the surficial aquifer, consists of gray fine to medium-sized sand and shell fragments. In addition, the LSU contains some isolated fine-grained lenses of silt and/or clay. The thickness of the underlying confining unit is unknown since boreholes are typically completed at the top of the clay unit to prevent drilling-induced migration from the LSU into the confined aquifer. The confining unit may act as a barrier to DNAPL migration into the confined aquifer.

The Atlantic Ocean is located immediately to the east of LC-34. To determine the effects of tidal influences on the groundwater system, water levels were monitored in 12 piezometers over a 50-

hour period during Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) activities (G&E Engineering, Inc., 1996).

All the piezometers used in the study were screened in the surficial aquifer. No detectable effects from the tidal cycles were identified in the subject area. However, the Atlantic Ocean and the Banana River (west of LC-34) are sufficiently close to the Site and appear to act as hydraulic barriers or sinks, as groundwater likely flows toward these surface water bodies and discharges into them. Other hydrologic influences at LC-34 include features such as paving, constructed drainage ditches, and topographical relief. Permeable soils exist from the ground surface to the water table and drainage is excellent. Water infiltrates directly to the water table.

Only limited data was available to characterize background geochemistry at LC-34 (Battelle, 1999; CRA, 1999) prior to the sequential technology demonstration. As may be expected, the salinity of groundwater in the surficial units (USU, MFGU, and LSU) increases with depth with concentrations of total dissolved solids as high as 1,200 milligrams per liter (mg/L) in the LSU (predominantly Na, K, Mg, Ca, Al, Cl, and total SO_4/S). Groundwater pH is near neutral (7.3-8.0) with an alkalinity of up to 360 mg/L (as $CaCO_3$). Although no direct measurements of oxidation-reduction potential are available, the high concentrations of dissolved iron and manganese indicate that the groundwater redox potential is generally reducing.

Following the ISCO demonstration at LC-34, the residual permanganate remaining in the test plot likely continued to slowly react with soil and/or residual TCE present in the subsurface while slowly migrating down-gradient of the test plot. Permanganate was not observed during a groundwater monitoring event (October 2002) conducted using monitoring wells located in and adjacent to the test plot, suggesting that the residual permanganate was depleted, which was an essential step prior to initiating treatment via bioremediation.

5.3 CONTAMINANT DISTRIBUTION

Pre- and post-treatment soil sampling was performed by Battelle during the previous technology demonstrations (Battelle, 2001a). The results of post-treatment monitoring in the ISCO test plot indicate that there 844 kg of total TCE mass, including 637 kg of TCE DNAPL, remained in the LSU.

A preliminary site investigation was conducted by Geosyntec in December 2002 to facilitate selection of locations for the ISCO pilot demonstration. Five boreholes were drilled within the ISCO PTA adjacent to the ESB to characterize the geology and the soil and groundwater chemistry. Soil samples from five boreholes were submitted for laboratory analysis of VOCs. The presence of DNAPL was inferred based on photoionization detector (PID) readings exceeding 9999 parts per million by volume (ppmv) and concentrations of TCE in soil exceeding 10,800 milligrams per kilogram (mg/kg). A detailed summary of the preliminary Site investigation is provided in Appendix A of the ER-0116 Final Report.

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6.0 TEST DESIGN

This section describes the design and the results of the demonstration test. Section 6.1 presents a conceptual experimental design; Section 6.2 describes the baseline characterization that was conducted; Section 6.3 describes the results of treatability and laboratory studies; Section 5.6 describes the field testing that was conducted; Section 6.5 describes the sampling methods; and Section 6.6 presents the results of the sampling conducted to monitor the field demonstration.

6.1 CONCEPTUAL EXPERIMENTAL DESIGN

The study approach consisted of a field trial to demonstrate that biostimulation and/or bioaugmentation can stimulate complete dechlorination of a nontoxic product (i.e., providing a contaminant mass containment) and evaluate whether the mass flux from a source zone increases when biological dehalorespiration activity is enhanced through nutrient addition and bioaugmentation (i.e., providing a secondary source removal technology post-ISCO). The layout of the pilot test cell is presented in Figure 4, and Figures 3-4 and 3-5 of the Final Report provide additional details regarding the process flow diagram of the system and the locations of the multilevel points.

The demonstration of the technology was designed to be completed in three operational phases: (1) baseline with groundwater circulation alone, (2) biostimulation with the addition of electron donor, and (3) bioaugmentation with the addition of electron donor and bioagumention with KB-1™. During the demonstration, groundwater was recirculated through the PTA at a constant groundwater velocity. Each phase was operated for sufficient duration to establish a near steady-state rate of TCE removal under each of the different operating conditions. The results of groundwater monitoring as well as laboratory microcosm studies using site materials from each operational phase were used to evaluate the performance of the technology.

6.2 BASELINE CHARACTERIZATION

6.2.1 VOC Characterization

Detailed measurements of the mass of TCE in the demonstration plot were not performed. The volume of the demonstration plot was 12,500 ft^3. Based on the average bulk concentrations of TCE in soil samples (836 mg/kg) collected from the PTA during baseline characterization, the total mass of TCE was approximately 370 kg prior to initiation of recirculation.

6.2.2 Test Plot Microbial Characterization

Only limited data was available characterizing the microbial population at LC-34 prior to the sequential technology demonstration. Prior to the oxidation demonstration, Eddy-Dilek et al. (1998) analyzed a limited number of soil and groundwater samples collected from the vicinity of ESB (in and outside of the DNAPL source zone) using heterotrophic plate and acridine orange enumeration techniques. While the limited number of samples precluded a definitive comparison, Eddy-Dilek et al. (1998) reported that the plate and acridine orange direct counts of

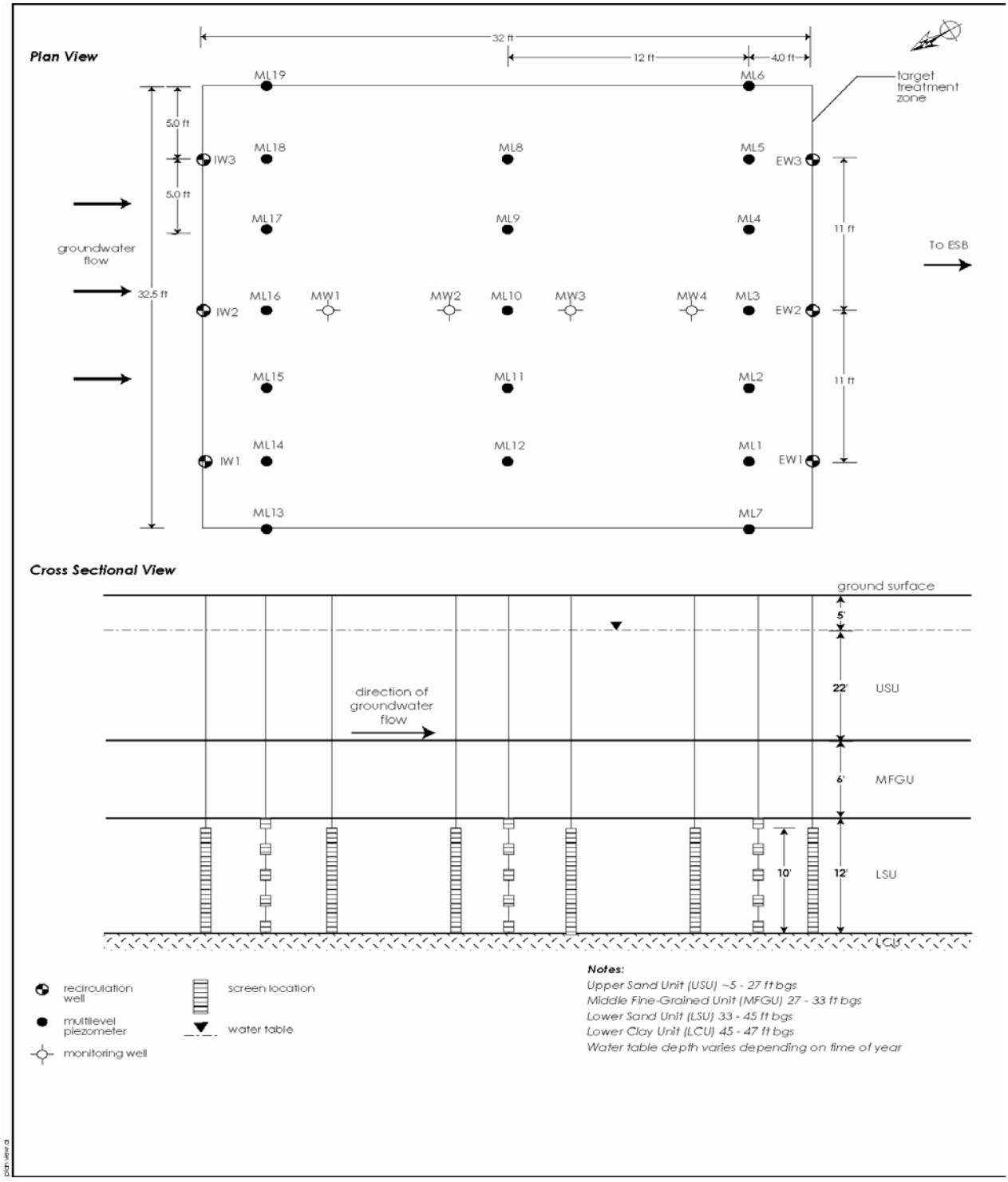


Figure 4. Instrumentation of PTA at Launch Complex 34.

samples collected from outside the source zone were consistent with a normal range; however, presence of DNAPL may inhibit microbial growth. There is some evidence available to suggest that *D. ethenogenes* are present in groundwater at LC-34. In May 2001, Geosyntec submitted groundwater samples from two monitoring wells to Dupont Laboratories, in Delaware, for analysis using molecular genetic techniques to detect the presence of these dechlorinating microorganisms and determined that *Dhc* bacteria are present in both background and plume samples. Subsequent samples submitted to SiREM Labs (in Guelph, Ontario, Canada) indicated that *Dhc*-like bacteria were present in five of six groundwater samples collected from the source area.

Further characterization of the soil microbial community at LC34 was carried out on samples from five soil cores collected in February 2003. Measurements of total phospholipid fatty acids (PLFA) (Microbial Insights, Rockford, TN) indicated an average of 115 picomoles PLFA/g dry weight, corresponding to an estimated cell density of 2.3×10^6 cells/gram of soil. Heterotrophic plate counts (GAP Enviromicrobial Services, London, ON) were significantly lower with maximum values of 8700 colony forming units/ gram (CFU/g) and anaerobic plate counts with maximum values of 11,300 CFU/g. Most probable number analysis (GAP) indicated negligible concentrations of sulfate-reducing organisms while targeted polymerase chain reaction (PCR) for the domain Archaea (SiREM, Guelph, ON) indicated the absence of DNA belonging to methanogens. Instead of sulfate reducers and methanogens the microbial community was dominated by members of the division Proteobacteria, specifically several *Pseudomonas* species, based on denaturing gradient gel electrophoresis (DGGE) analysis (SiREM). Furthermore, targeted PCR indicated the presence of dechlorinating *Dhc* group organisms, with microcosm studies (SiREM) confirming the ability of the soil microorganisms to mediate complete dechlorination of TCE to ethene, suggesting that viable *Dhc* populations were present. A summary of these data is provided in Appendix M of the ER-0116 Final Report.

6.2.3 Hydraulic Characterization

A groundwater tracer test was conducted using a conservative solute (NaBr) to evaluate flow conditions within the PTA. Details of the methods and results of the tracer tests are provided in Appendix D of the Final Report. Based on the results of the tracer tests, the average linear velocity from the monitoring wells was 1 ft/day, which provides a residence time along the center line of the PTA of 32 days (using the length of 32 ft, 2 inches). Analysis of tracer arrival at the multilevel wells suggests that the arrival of electron donor and any reinjected VOCs will not be uniform across the PTA at the Fence 1 multilevel wells but should be fairly uniform at the Fence 2 and Fence 3 multilevel wells.

Hydraulic response tests of IW-2 and IW-3 were completed on July 30,2003, to determine the hydraulic conductivity of the LSU. The results from these tests were interpreted using Aquifer Test 3.0 (Waterloo Hydrogeologic) and are summarized in Appendix E of the ER-0116 Final Report. The average hydraulic conductivity was 7×10^{-6} meter per second (m/s) (2 ft/day).

6.2.4 Electron Donor Demand

Baseline concentrations of electron acceptors in groundwater and electron donor demand calculations are summarized in Table 4-3 of the ER-0116 Final Report, resulting in a

stoichiometric electron donor demand of 107 mg/L (as ethanol). The majority of the donor demand was exerted by sulfate (74 mg/L as EtOH). Assuming a unit volume of soil (1 m^3, porosity 0.33), the total electron donor demand of the soluble acceptors corresponds to 35 grams (g) of ethanol. However, manganese dioxide in soil (average concentration soil of 7224 mg/kg, bulk density 2000 kg/m^3) is also a significant electron acceptor: in a unit volume of soil, the electron donor demand of the insoluble manganese dioxide corresponds to 853 g of ethanol. Accordingly, the presence of manganese dioxide in the Test Plot results in a 25-fold increase in the electron donor dosing requirements.

6.3 TREATABILITY AND LABORATORY STUDY RESULTS

Prior to initiating the demonstration, a number of pre-demonstration tasks were completed to collect essential data required to effectively implement this technology demonstration. As described in the following sections, these tasks include predesign chemical and microbiological laboratory testing (Section 6.3.1) and University of Toronto (UT) laboratory studies (Section 6.3.2).

6.3.1 Predesign Treatability Studies

A series of predesign treatability studies were performed to:

- Assess the effect of manganese dioxide on the utilization of common electron donors by indigenous microorganisms
- Determine if manganese dioxide reacts via an abiotic pathway with common electron donors at significant rates
- To evaluate the impact of permanganate addition on enhanced biodegradation of TCE in groundwater
- Measure the natural oxidant demand of soil at the demonstration site.

The design, methods used, and results of these studies are provided in Appendix B of the Final Report. These studies resulted in the following conclusions:

- Permanganate treatment did not significantly inhibit the utilization of electron donors by fermenting bacteria in microcosms.
- Neither ethanol, methanol, glucose, lactate, glycol nor acetate were abiotically oxidized by manganese dioxide at a significant rate; however, manganese dioxide reacted rapidly with oxalic acid.
- Complete dechlorination occurred only in microcosms bioaugmented with KB-1. However, stoichiometric conversion of the amended TCE to ethene was slower in microcosms that were pretreated with permanganate.

- The average oxidant demand of the LC-34 soil was 2.3 g-$KMnO_4$/kg over 72 days.

- There was no evidence of abiotic chloroethene or ethene oxidation by manganese dioxide at environmentally significant rates.

6.3.2 University of Toronto Column Studies

Column studies examining the sequential application of ISCO and ISB were completed at the University of Toronto. The design of these studies, the methods used and results of the column studies are provided in detail in Appendix C of the ER-0116 Final Report. These studies resulted in the following conclusions:

- Rebounding of TCE concentrations following oxidation indicates that a polishing technology (such as ISB) is required.

- The addition of bacteria, either through the ambient movement of site groundwater or bioaugmentation, may be required to restore microbial activity following oxidant treatment.

- The inoculation of dechlorinating cultures into oxidized conditions may impair the ability of the culture to subsequently degrade *cis*-1,2-dichloroethene (*cis*-DCE), even when reducing conditions are reestablished.

- Columns bioaugmented prior to the onset of manganese-reducing conditions could only dechlorinate TCE to *cis*-DCE; however, complete dechlorination to ethene occurred in columns bioaugmented after the onset of manganese-reduction.

6.4 FIELD TESTING

Details of the construction of the treatment system, field methods, and approach are described in detail in the Final Report for the demonstration (Geosyntec, 2009). The demonstration was constructed in 2003 and operated between June 2003 and August 2004.

The treatment system includes injection and extraction wells, the aboveground treatment system, process instrumentation, and process controls. The locations of monitoring and recirculation wells are presented in Figure 4. The process flow diagram of the aboveground recirculation system and a conceptual cross-sectional diagram of the multilevel transects are presented in Figures 3-4 and 3-5 of the ER-0116 Final Report.

The demonstration of the technology was designed to be completed in three operational phases. Baseline operation started on December 8, 2003. Biostimulation (addition of electron donor to increase the activity of the indigenous microorganisms and stimulate dechlorination) began March 1, 2004. On April 15, 2004, the PTA was bioaugmented with KB-1™, a bacterial consortium containing *Dhc* species (bioaugmentation). Ethanol amendment was continued during the bioaugmentation phase. It was intended that the demonstration would continue longer to test the hypothesis that the ethene would eventually become the predominant dechlorination

product; however, system operation was severely impacted by a series of hurricanes and the demonstration was terminated in August 2004.

Following the completion of the demonstration, a final round of groundwater samples was collected from the center line monitoring wells (August 2005). At this time, the system had been shut down for 12 months.

The approach used to meet the project objectives was to compare VOC/dissolved hydrocarbon gas (DHG) concentrations and the mass discharge of VOCs from the test plot during the baseline, biostimulation, and bioaugmentation phases of the study. It was anticipated that amendment of the PTA would result in reductive dechlorination of TCE to ethene (i.e., decreasing TCE concentrations) and increase VOC mass discharge. Prior to the baseline phase, tracer tests were performed to determine groundwater velocities.

6.5 SAMPLING METHODS

Samples were collected and analyzed following protocols established in the Technology Demonstration Plan and described in the Section 3.5.8 of the Final Report and in the Sampling and Analysis Plan, Quality Assurance Plan and Analytical Methods Appendices (F, G, and H) of the Final Report. Laboratory Analytical methods used during the demonstration are summarized in the Final Report, Table 3-3, and detailed descriptions of the analytical methods employed for VOC, DHG, volatile fatty acid (VFA), PLFA, anion, and metals analysis are provided in the Final Report, Appendix I.

6.6 SAMPLING RESULTS

6.6.1 Field Parameters and Geochemical Indicators

Field parameters (temperature, pH, specific conductance, and oxidation reduction potential [ORP]) for the center line monitoring wells are provided in the ER-0116 Final Report, Appendix K, and summarized in the Final Report, Figure 4-1. Key geochemical indicators (total VFA, manganese, and sulfate) are provided in the Final Report, Appendix L and summarized in Final Report Figure 4-2. Temperature in test plot monitoring wells ranged from 24°C (March 2004) to 29°C (October 2003), reflecting seasonal variation in surface temperatures. The specific conductance of test plot groundwater was ~3,500 microSiemen per centimeter (µS/cm) throughout the demonstration, which is considered a brackish groundwater (Freeze and Cherry, 1979). Initial environmental conditions in the test plot were anaerobic (ORP measurements ranging from 32 to -40 millivolts [mV], characteristic of Mn-reducing conditions (Wiedemeier et al., 1999), and slightly alkaline (pH measurements ranging from 8.1 to 9.2). During the biostimulation/bioaugmentation phases, both pH (final pH ranging from 7.4 to 7.6) and ORP (final ORP ranging -265 to -295 mV, characteristic of sulfate-reducing or methanogenic conditions [Wiedemeier et al., 1999]) decreased in the test plot.

Concurrent with these changes, the average concentration of total VFAs (representing a combined concentration of acetate and lactate) in these monitoring wells increased from 24 mg/L (baseline) to 453 mg/L (August 20, 2004) while the average concentration of sulfate decreased

from 883 mg/L (baseline) to 50 mg/L (August 20, 2004). This change indicates that the available electron donor was initially utilized for sulfate-reduction until the sulfate reservoir was depleted.

The maximum methane concentration observed during the baseline treatment phase was 0.3 mg/L. During electron donor addition (biostimulation/bioaugmentation) only a small increase in methanogenesis were observed. The absence of a significant increase in methane concentrations suggests that methanogenesis may have been inhibited by the high VOC concentrations (DiStefano et al., 1991).

The average baseline sulfate concentration in groundwater was 285 mg/L; the maximum concentration observed following electron donor addition was 11 mg/L with several nondetects, indicative of increases in the activity of sulfate-reducing microorganisms in groundwater.

The data collected suggest that electron donor amendment did not result in either iron or manganese reduction. No significant increase in the concentration of dissolved manganese, expected to be a significant sink for electron donor under these environmental conditions, appeared to occur during the demonstration (ER-0116 Final Report, Figure 4-2).

6.6.2 VOCs and DHGs

All VOC and DHG data are provided in the ER-0116 Final Report, Appendix L. Time-series plots presenting the concentrations of chloroethenes, ethane, and methane in the center line monitoring wells are presented in Figure 5. Average VOC and DHG concentrations during each demonstration phase are summarized in Table 3. Under intrinsic conditions (baseline), TCE, *cis*-DCE, and vinyl chloride (VC) were detected in test plot groundwater samples; however, the concentrations of *cis*-DCE (the dominant TCE degradation product in these samples) and VC represent only 16% of the total ethenes concentration. Ethene was not detected in any of the 12 baseline groundwater samples (<0.1 mg/L). The limited extent of reductive dechlorination of TCE under intrinsic conditions was likely limited by the absence of sufficient electron donor to overcome the significant electron donor demand exerted by other reductants (e.g., manganese and sulfate).

Table 3. Summary of PTA Geochemistry.

Phase	Date Collected	Concentration (mg/L)					
		TCE	*cis*-DCE	VC	Ethene	Methane	Sulfate
Baseline	19-Mar-04	94	61	0.8	0.2	0.2	273
Biostimulation	12-Apr-04	112	125	2	0.2	0.2	94
Bioaugmentation	18-Aug-04	14	140	42	0.5	0.5	50
Post-Demonstration	16-Aug-05	0.1	20	22	4	0.9	5

1. Post-demonstration groundwater samples were collected 12 months after system shut-down.
2. Concentrations represent the average result of groundwater samples collected from the center line monitoring wells at the end of each demonstration phase.

Following the start of the biostimulation phase, increased dechlorination of TCE to *cis*-DCE was observed, suggesting that organisms mediating TCE dechlorination to *cis*-DCE were present in the PTA. The addition of electron donor did not appear to stimulate methanogenesis. There was minimal dechlorination of *cis*-DCE to VC and/or ethene. Further dechlorination, including the

production of ethene at concentrations as high as 2.7 mg/L, occurred during the bioaugmentation phase (Figure 5).

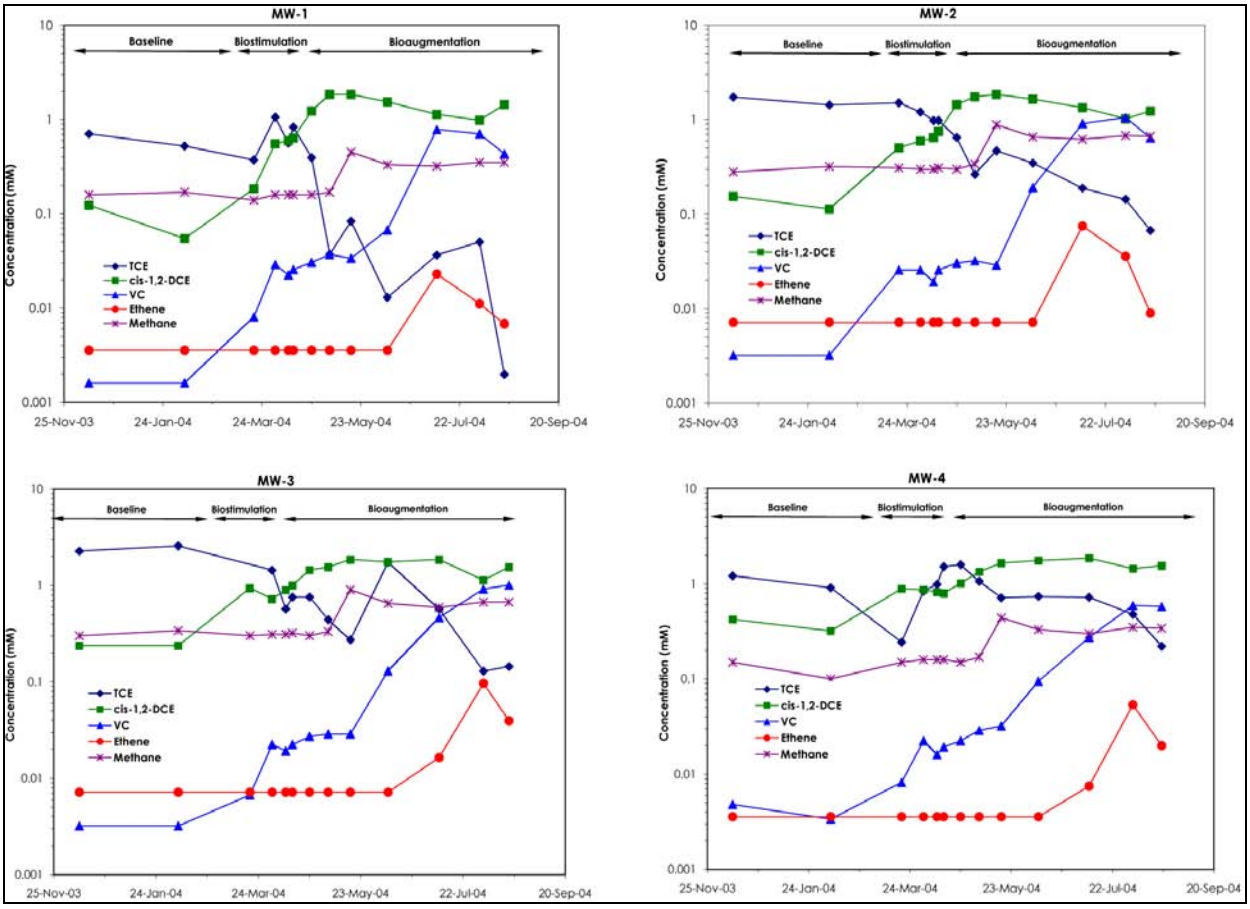


Figure 5. Chloroethene, ethene, and methane concentrations in center line monitoring wells.

The mean chloroethene mass flux at the downgradient fence of multilevel monitoring wells (Fence 3) is summarized in Figure 6. Chloroethene mass fluxes at Fence 3 ranged from 39 to 53 millimole per square foot per day (mmole/ft^2/day), corresponding to TCE removal rates of 2.5 to 3.6 kg/day. A significant increase in chloroethene mass flux was not observed during the demonstration. The extent of dechlorinating activity (given by the dechlorination score, which represents the mole fraction of chlorine removed from the initial concentration of the parent compound) at Fence 3 is summarized in Figure 7 using box-and-whisker plots. The dechlorination score (N_D) is given by:

$$N_D = \frac{[cisDCE] + 2[VC] + 3[Ethene]}{3([TCE] + [cisDCE] + [VC] + [Ethene])}$$

where the values in parentheses represent molar concentration units and scores of 0.33 and 0.66 represent complete conversion to equivalent concentrations of *cis*-DCE and VC, respectively. Figure 7 represents the summary statistics (range, 25th and 75th percentiles, and median) for each complete round of samples collected from Fence 3. Although in each sample event there is a large range of scores, the dechlorination scores for the baseline and biostimulation sample events indicate that there is relatively little dechlorination of TCE and that it results in the accumulation of *cis*-DCE. However, the median dechlorination score of samples collected for the bioaugmentation sample event (0.32) indicate that there was a shift in the extent of reductive dechlorination past *cis*-DCE by the end of the bioaugmentation phase. This is evident in the distributions of dechlorination products shown in Figure 6, which illustrates that the bioaugmentation sample event was unique in that it was the only sample event in which cDCE concentrations exceeded TCE concentrations and it had the highest concentrations of VC and ethene. This shift in the extent of dechlorination was confirmed in the post-demonstration sampling event (ER-0116 Final Report, Table 4-4). The maximum ethene concentration in this sampling event was 10 mg/L (MW-1).

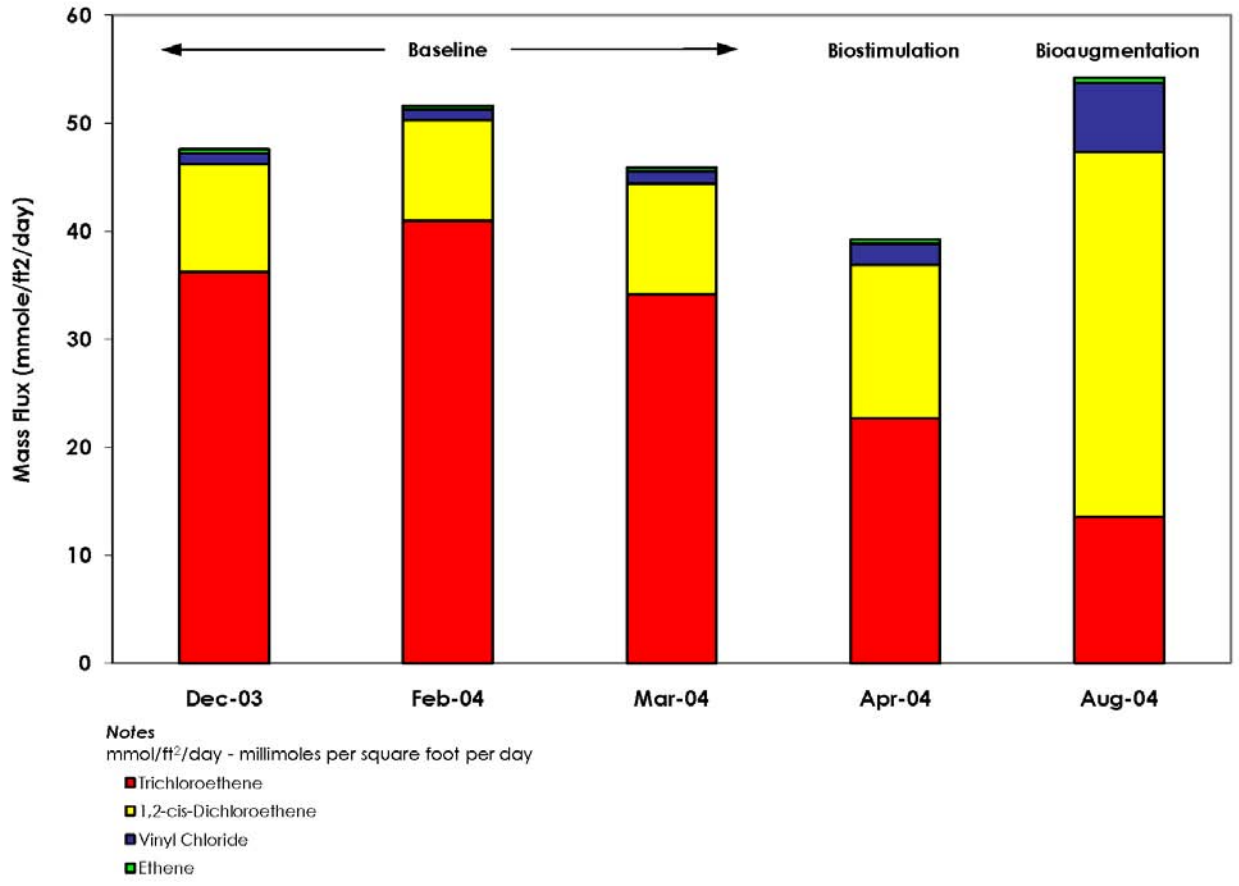
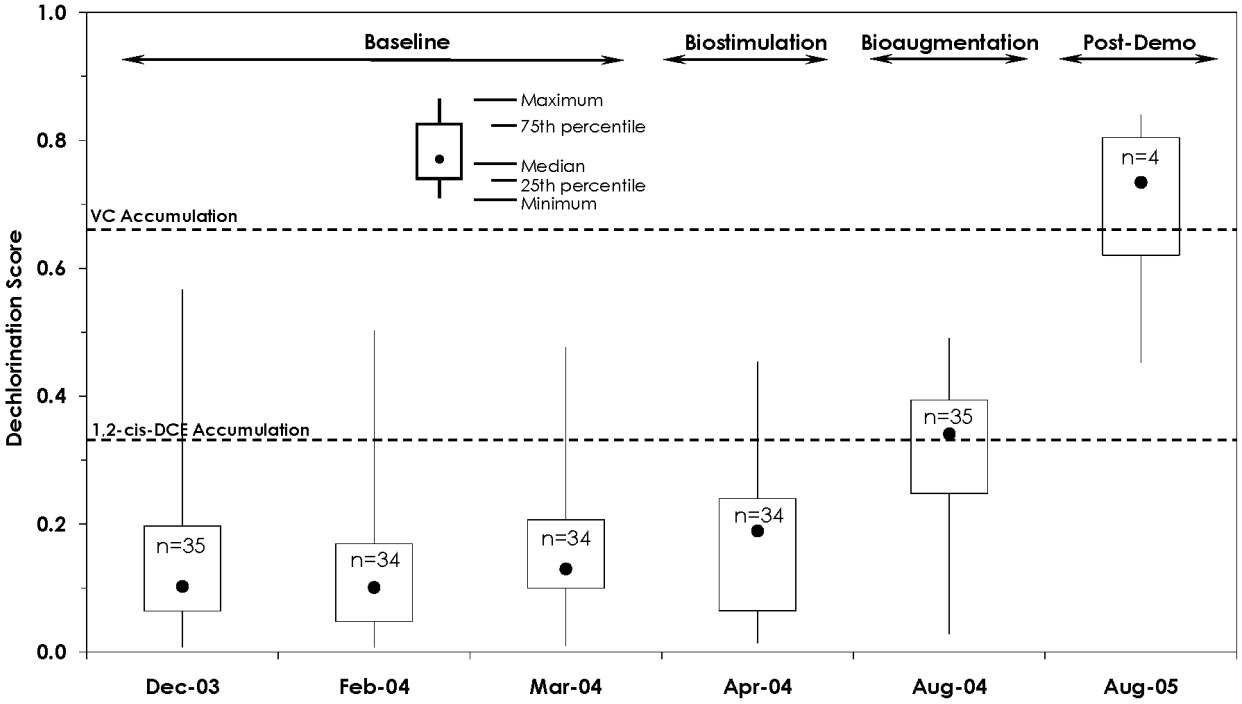


Figure 6. Mass flux of chloroethenes and ethene in groundwater at Fence 3.



Notes
1. Dechlorinating scores represent the molar fraction of chlorine removed from the initial concentration of the parent compound (i.e., TCE), which is equal to the total ethenes concentration,
2. Dechlorination scores calculated using data from all Fence 3 sampling locations, with the exception of the Aug-05 event (monitoring wells only).

Figure 7. The extent of dechlorination at Fence 3.
(Dashed lines at 33 and 66% represent complete conversion of the parent TCE to either *cis*-DCE or VC, respectively.)

6.6.3 Chloroethene and Ethene Concentrations/Mass Discharge

Concentrations of chloroethenes and ethene in the extracted groundwater are summarized in Figure 8. These concentrations reflect mixing of groundwater containing TCE from both the PTA and from the surrounding aquifer. The concentrations of chloroethenes and ethene indicate that 20% of the parent TCE in the extracted groundwater was converted to cDCE and VC during the baseline phase. No detectable concentrations of ethene were observed during baseline.

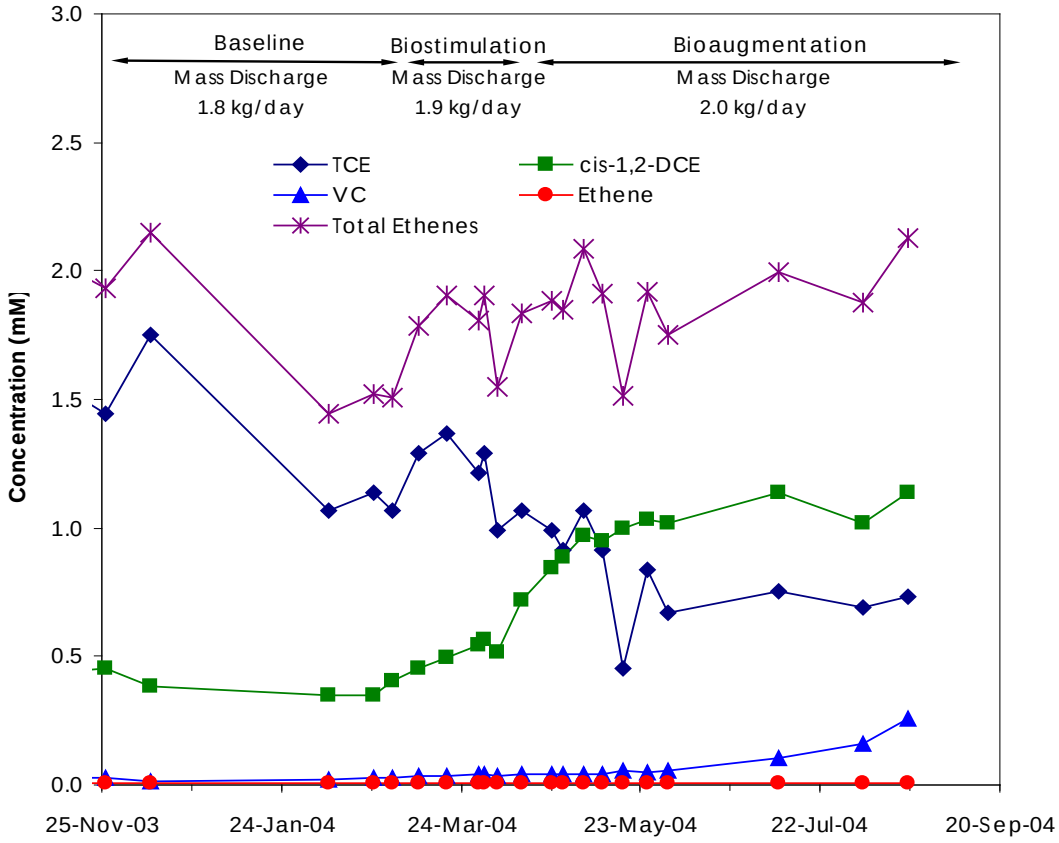


Figure 8. Chloroethene and ethene concentrations in extracted groundwater.

During biostimulation, changes in the proportions of the less-chlorinated degradation by-products observed in the extracted groundwater were consistent with the changes observed in the center line monitoring wells. Following electron donor addition, increases in the concentration of cDCE were followed by increases in VC concentrations corresponding to 31% molar conversion of the parent TCE concentration. No detectable concentrations of ethene were observed during biostimulation. During the bioaugmentation phase, further increases in the concentration of cDCE, VC, and ethene occurred, corresponding to 56% molar conversion of the parent TCE concentration. The maximum ethene concentration in the extracted groundwater was 0.3 mg/L.

The total chloroethene mass discharge in the extracted groundwater during the baseline, biostimulation, and bioaugmentation phases was 1.8, 1.9, and 2.0 kg/day (as TCE), respectively. A significant increase in the mass discharge did not occur during the demonstration.

6.6.4 Microbial Characterization

An extensive program of microbial characterization was completed using samples collected at the end of the baseline, biostimulation, and bioaugmentation phases of the demonstration. Detailed reports for each of these three studies are included in the ER-0116 Final Report, Appendix M.

Key results of the baseline microbial characterization study, using samples collected from the Test Plot and a background Control Plot, include:

- Biomass density in the Test Plot appears to be approximately two-fold higher than the biomass density in the Control Plot.
- There were significant differences in the microbial community structure between the Test and Control Plots. The Test Plot community includes members of the *Acinitobacteria*, *Acidovorax*, and *Symbiobacterium*, which were not detected in the Control Plot. The microbial community in the Control Plot appeared to be dominated by members of the gamma subdivision of the Proteobacteria and, more specifically, Pseudomonas species, a number of which were not present in the Test Plot.
- DNA from *Dhc* organisms is present in the Test Plot; however, only bacteria from Control Plot samples exhibited dechlorinating activity. Dechlorination activity in the ISCO Test Plot was strongly inhibited, even after over 276 days of incubation.

Key results of the biostimulation microbial characterization study include:

- As anticipated, the shift in trophic conditions (e.g., substrate availability) resulted in a decrease in overall microbial diversity.
- The microbial population is dominated by bacteria, with no evidence of methanogenic organisms.
- *Dhc* microorganisms were not detected; however, organisms at two thirds of the sample locations completely dechlorinated TCE to ethene, indicating that these organisms were present at an initial cell density below the detection limit of the *Dhc* PCR method. Methanogenesis occurred concurrently in these samples with TCE dechlorination to ethane.
- In a third sample, which contained visible MnO_2, dechlorination and methanogenesis were completely inhibited over 70 days of incubation.

Key results of the bioaugmentation microbial characterization study include:

- There was no evidence of a further significant shift in the diversity of the microbial community. The total biomass density appeared to slightly increase.
- The microbial population is dominated by bacteria. Targeted PCR assays for Archaea were negative, consistent with an ongoing absence of methane.
- Targeted PCR assays for *Dhc* indicate that this organism was present in two thirds of the samples. Microorganisms at these samples completely dechlorinated TCE to ethene. Methanogenesis occurred concurrently in these samples with TCE dechlorination to ethane.
- In a third sample containing MnO_2, dechlorination and methanogenesis were completely inhibited over 84 days of incubation.

6.6.5 Field Demonstration Conclusions

The field demonstration resulted in the following conclusions:

- Ethanol fermentation occurred rapidly, and fermentation products (such as acetate and lactate) were distributed throughout the Test Plot.
- Sulfate reduction occurred rapidly after the start of electron donor addition.
- Biodegradation of TCE to *cis*-DCE, and to a much lesser extent to vinyl chloride, occurred following electron donor addition. Concentrations of TCE decreased significantly during the demonstration and were nondetect in the post-demonstration sampling event.
- Additional dechlorination occurred following Test Plot bioaugmentation, resulting in the formation of vinyl chloride and to a much lesser extent to ethane.
- A small increase in methane concentration occurred during following Test Plot bioaugmentation (average concentration 0.5 mg/L).

It was intended that the demonstration would continue longer to test the hypothesis that the ethene would eventually become the predominant dechlorination product; however, system operation was severely impacted by a series of hurricanes and the demonstration was terminated.

6.6.6 Key Geochemical Processes

In addition to the decreases in ORP measurements to levels characteristic of sulfate-reducing/methanogenic activity, there was strong evidence of anaerobic microbial processes usually associated with reductive dechlorination, including fermentation, manganese reduction, and sulfate reduction. Fermentation was evident by the rapid disappearance of ethanol and the appearance of typical fermentation products (including acetate, lactate, propionate, and butyrate). Although there were no significant increases in dissolved manganese concentrations (ER-0116 Final Report, Figure 4-2), soil samples collected for the microbial characterization studies provided evidence of manganese reduction. While the color of baseline soil samples (dark brown to black) was characteristic of manganese dioxide, subsequent soil samples from the same locations were light gray, indicating that the manganese dioxide had been depleted by manganese reduction and that the manganese was now present in other mineral forms (e.g., reduced manganese mineral species, sorbed to other mineral surfaces). Declines in sulfate concentration were indicative of sulfate reduction by indigenous test plot microorganisms, although sulfate was not entirely depleted (ER-0116 Final Report, Figure 4-2). Interestingly, there was no evidence of methanogenesis, although ORP measurements (typically less than -240 mV during the biostimulation/ bioaugmentation phases) indicated that the environmental conditions would support this process (Wiedemeier et al., 1999). The inhibition of methanogenesis may result from the presence of high chloroethene concentrations, competitive electron donor utilization by other reduction processes (especially manganese reduction), and the absence of methanogenic bacteria (as determined by Archeae-specific molecular testing). In conjunction with the microbial diversity studies and consistent with data reported by Azadpour-Keely et al. (2004), it is evident that the PTA was rapidly recolonized in the 3 years following permanganate amendment by a diverse microbial community.

Although the addition of electron donor resulted in environmental conditions suitable for manganese reduction, the absence of appreciable increases in dissolved manganese concentrations during the demonstration suggest that the transport of reduced manganese (Mn^{2+}) was limited. The results of geochemical modeling (ER-0116 Final Report, Appendix J) suggest that the presence of sufficient sulfate favors the precipitation of reduced manganese (Mn^{2+}) as alabandite (MnS). Other significant controls on dissolved Mn transport in groundwater include cation exchange onto manganese dioxide surfaces, precipitation as MnO_2, and precipitation as $MnCO_3$ (Stumm and Morgan, 1970).

These data suggest that the deposition of manganese dioxide during ISCO has important consequences on the performance of subsequent efforts to promote reductive dechlorination. Manganese reduction is thermodynamically favored in comparison to dechlorination (ER-0116 Final Report, Figure 4.7) and exerts an electron donor demand in significant excess of that required solely to support reductive dechlorination, increasing the quantity of electron donor required for source area treatment. In comparison to *Dhc* microorganisms that are necessary for cDCE and VC dechlorination to ethene, manganese reducing microorganisms rapidly utilize hydrogen, the sole electron donor for reduction of these chloroethenes. The reported hydrogen threshold for manganese-reduction is <0.1 millimolar (mM); however, the reported thresholds for reductive dechlorination range from 2 to 11 mM (AFCEE, 2004). Accordingly, highly efficient hydrogen utilization by manganese-reducing microorganisms appears to inhibit dechlorination by maintaining the hydrogen concentration below the minimum threshold required to support reductive dechlorination of cDCE and VC.

7.0 PERFORMANCE ASSESSMENT

7.1 PERFORMANCE CRITERIA

The performance of the demonstration was evaluated using the general performance criteria provided in Table 4. Qualitative and quantitative criteria are classed as either primary or secondary performance assessment criteria, respectively.

The primary criteria constitute the performance objectives of the technology demonstration. As stated in Section 2.2 and further described in Section 4, the general objectives of the demonstration were to evaluate the impacts of ISCO on the native microbial community, determine if ISB is feasible following ISCO implementation, and whether bioaugmentation enhances VOC degradation post-ISCO. In general, the performance criteria were used to evaluate these objectives by:

- Determining the ability of the native and bioaugmented microbial consortia to colonize the remaining source zone and test area post-ISCO
- Quantifying the effect of the technology on the mass flux from the source zone
- Quantifying the effect of the technology on VOC degradation rates
- Assessing the potential benefits of bioaugmentation
- Evaluating the difficulty in implementing this technology at the field scale.

7.2 PERFORMANCE CONFIRMATION METHODS

The success of the technology demonstration was evaluated using the performance expectations and confirmation methods presented in Table 5. Successful implementation of the technology would demonstrate that the technology results in significant post-ISCO microbial activity, a statistically significant increase in the degradation rate of aqueous TCE with rapid and complete degradation to ethene. As a consequence of the microbial activity and VOC degradation, the rate of TCE DNAPL removal would increase as compared to pump-and-treat, decreasing the duration of remediation required for complete restoration of the PTA.

It was intended that the demonstration would continue longer to evaluate the technology; however, system operation was severely impacted by a series of hurricanes and ultimately the demonstration was terminated. Despite this early termination of the demonstration, the data gathered was sufficient to evaluate the performance objectives of the demonstration and following assessment was made.

Table 4. Performance criteria.

	Performance Criteria	Description Criteria
Primary	Microbial activity in source zone	The ability of the indigenous and inoculated consortia to colonize the source zone after oxidant treatment is essential for the coupling of oxidation and bioremediation technologies.
	Extent of dehalogenation	Dehalogenation of TCE will indicate activity of microorganisms capable of degradation. Complete degradation of TCE to ethene will limit the mobility of the chlorinated daughter products.
	Mass flux from DNAPL	Rate that mass is removed from DNAPL by remedial technology; presence of DNAPL mass requires remediation of the groundwater plume over a period of decades to centuries.
Secondary	TCE degradation rate	Degradation of the parent compound (TCE) will enhance the rate of DNAPL removal; rapid DNAPL dissolution decreases length of remediation. Degradation rate may be impacted by microbial inhibition via post-oxidation geochemical conditions.
	Duration of remediation	Time required to remove the source zone using enhanced bioremediation/bioaugmentation relative to flushing with unamended groundwater (base case treatment). Estimated based upon a comparison of TCE concentration in initial boreholes and mass flux data.
	Factors affecting performance > Location and amount of biomass injected into PTA	Creating a zone of highly active dehalogenating biomass in the immediate vicinity of the DNAPL is of critical importance; colonization of dehalogenating microorganisms is influenced by specifications of innoculum, location of injection point, and concentration of electron donor at injection point.
	> Location and concentration of electron donor injected into PTA	Electron donor is anaerobically fermented to produce hydrogen (the primary substrate), which can be utilized by non-dehalogenating microorganisms; need to ensure that electron donor is supplied to active dehalogenators in the source zone.
	> Geologic heterogeneity	The presence of low permeability zones may limit delivery of both the inoculum and electron donor to the source zone.
	> Post-oxidation geochemical conditions	Elevated pH, highly oxidizing conditions, and manganese species may inhibit microbial activity.
	Implementation issues > Maintenance requirements	One operator with minimal additional training is required for occasional visits during the demonstration; weekly adjustments and maintenance will be needed in addition to sample collection.
	> Reliability	Operation of system expected to be highly reliable and capable of operating without the need for a full-time operator.
	Mobility of groundwater plume	As the source material is removed, the plume will be reduced.
	Appropriate pH & redox conditions	Near neutral pH (or near site background), low dissolved oxygen concentration and oxidation-reduction potential are required to permit an increase in the acidity of the dehalogenating microorganisms.

Notes:
PTA – Pilot Test Area
DNAPL – Dense Non-Aqueous Phase Liquid
TCE - Trichloroethene

Table 5. Expected performance and performance confirmation methods.

	Performance Criteria	Expected Performance Metric	Performance Confirmation Method	Actual
Primary Criteria	**Qualitative**			
	Microbial activity in source zone	Increase in the concentration of biomass and extent of colonization of source by indigenous and bioaugmented consortia	PLFA, *Dhc*, and DGGE analysis; aerobic and anaerobic plating; microcosms to confirm degradation rates	Significant microbial activity was present throughout the demonstration. Organisms present during the baseline phase did not dechlorinate TCE; apparent inhibition of dechlorination in the presence of manganese dioxide during biostimulation & bioaugmentation phases (ER-0116 Final Report, Appendix I)
	Extent of dehalogenation	Complete dehalogenation to ethene	Analysis of groundwater samples for TCE and TCE daughter products	Minimal dechlorination during baseline; dechlorination to *cis*-DCE, VC, and ethene during the biostimulation and bioaugmentation phases (Figures 5, 6, and 7)
	Quantitative			
	Mass flux from DNAPL -After amendment with electron donor (biostimulation)	Increase in mass flux above the base case treatment	Measurement of the concentrations of VOCs, ethene; calculation of mass flux	No significant increase in mass flux (Figure 6)
	-After bioaugmentation	Increase in mass flux above the relative to biostimulation		No significant increase in mass flux (Figure 6); however, mass flux of dechlorination products exceeded that of the parent TCE
Secondary Criteria	**Qualitative**			
	TCE degradation rate	Increase in degradation rate following bioaugmentation	Interpretation of trend and distribution of VOCs, ethene, in groundwater	Increases in the rate of *cis*-DCE and VC production following electron donor addition
	Duration of remediation	Decrease in overall remedial duration as a result of increased mass flux during ISB	Interpretation of mass flux data and initial mass in boreholes	Mass flux did not increase significantly over the demonstration (from 1.8 kg/day to 2.0 kg/day TCE) so that remedial duration would not be substantially shorter

Table 5. Expected performance and performance confirmation methods (continued).

	Performance Criteria	Expected Performance Metric	Performance Confirmation Method	Actual
Secondary Criteria	**Qualitative**			
	Factors affecting performance			
	-Location and amount of biomass injected into test plot	Mobility of biomass may be limited in porous media; accumulation of biomass in the source zone preferred	Experience from operation of demonstration; collection of samples for microbial characterization	Not evaluated; a small increase in biomass density was observed
	-Location and concentration of electron donor injected into test plot	Electron donor may be preferentially consumed by biomass without stimulating dehalogenation of chlorinated ethenes	Experience from operation of demonstration; collection of groundwater samples and analysis of electron donor concentrations	Evidence of significant sulfate reduction; minimal methanogenesis during the demonstration
	-Geologic heterogeneity	Low permeability may limit the delivery of electron donor and biomass to the source	Experience from operation of demonstration; tracer testing and soil sampling	Not evaluated except at injection wells; permeability reductions during due to biofouling
	-Post-oxidation geochemical conditions	High pH, high manganese concentrations, oxidizing conditions may inhibit microbial activity	Measurement of the concentrations of Mn, field parameters (pH level, ORP, dissolved oxygen)	Some evidence (via microcosm studies) that high manganese concentrations (MnO_2) inhibited reductive dechlorination
	Implementation issues			
	-Maintenance requirements	Replacement of tubing in peristaltic pumps; adjustment of injection level control system; replenishment of amendments	Evaluation of maintenance records and daily field logs	Implementation of biofouling control measures were the only significant maintenance requirement
	-Reliability	Fraction of time system is shut down (zero flow)	Evaluation of system operational records	Significant downtime due to biofouling and hurricane damage

Table 5. Expected performance and performance confirmation methods (continued).

	Performance Criteria	Expected Performance Metric	Performance Confirmation Method	Actual
Secondary Criteria	**Quantitative**			
	Mobility of groundwater plume	Decrease in the steady-state plume length	Calculating based on simulated steady-state plumes using degradation rates estimated from test plots	Not assessed due to small size of demonstration plot
	Achieve appropriate geochemical (pH, Redox, Mn, Fe) conditions	Anaerobic and reducing groundwater in test cell; pH at neutral/background levels; minimize Mn and Fe dissolution (which would lead to fouling)	Field measurement of pH, dissolved oxygen, ORP, Mn, Fe	Highly reducing conditions achieved (see Section 6.6.1)

Notes:
DNAPL – dense non-aqueous phase liquid
TCE - Trichloroethene
PLFA – phosopholipid fatty acid analyses
Dhc – Dehalococcoides
DGGE – denaturing gradient gel electrophoresis
VFAs – volatile fatty acids
Mn – manganese
Fe - iron

7.2.1 Microbial Activity in the Source Zone

Significant microbial activity was present throughout the demonstration. Organisms present during the baseline phase did not dechlorinate TCE, despite the presence of *Dhc* in the Test Plot. However, in microcosms using materials from the Test Plot during the biostimulation and bioaugmentation phases, dechlorination through to ethane was observed concurrent with methanogenesis, which was consistent with dechlorination activity observed in the PTA. *Dhc* was measured using targeted PCR assays in bioaugmentation samples. There was an apparent inhibition of dechlorination in the presence of manganese dioxide during biostimulation and bioaugmentation phases (ER-0116 Final Report, Appendix I).

7.2.2 Extent of Dehalogenation

The extent of dehalogenation increased over the course of the pilot study, with *cis*-DCE and VC concentrations increasing in the biostimulation phase and further increasing in the bioaugmentation phase. Ethene concentrations were highest in the bioaugmentation phase and in post-treatment sample events. Correspondingly, the dechlorination score increased from baseline through biostimulation and bioaugmentation (where cDCE accumulation was observed) and was highest post-demonstration, with VC accumulation observed.

7.2.3 Mass Flux from DNAPL

The total chloroethene mass discharge in the extracted groundwater during the baseline, biostimulation, and bioaugmentation phases was 1.8, 1.9, and 2.0 kg/day (as TCE), respectively. Similarly, the chloroethene mass flux also did not increase significantly during the demonstration, although the mass flux of dechlorination products (cDCE, VC, ethene) did increase over the demonstration, so that these were the dominant compounds present during the bioaugmentation phase. Mass flux enhancement during ISB has been reported previously at LC-34 in a separate demonstration (up to four-fold) (Hood et al., 2008) and other sites (three- to six-fold) (Christ et al., 2005) but has not been widely evaluated for ISB following ISCO. Potential reasons for the limited mass flux enhancement observed during ISB for this demonstration include (1) the shortened duration and downtime during the field test due to hurricanes and operational difficulties; (2) extracted groundwater from outside the PTA influencing mass estimates; and (3) manganese dioxide precipitates limiting mass transfer from any remaining DNAPL. A definitive evaluation of the ability of ISB to enhance mass flux following ISCO to achieve continued source treatment cannot be made from this demonstration. However, the increase in dechlorination product mass flux does suggest that a sequential ISCO-ISB remedy can allow plume containment, which would be beneficial in reducing plume extent and associated monitoring and remediation costs.

The limited duration of the demonstration makes it difficult to assess the DNAPL mass reduction and any overall changes to the remedial duration for this site.

7.2.4 TCE Degradation Rate

Degradation rates of TCE increased over the demonstration, as was illustrated in Figure 5 by the accumulation of cDCE, VC, and ethene in the biostimulation and bioaugmentation phases.

7.2.5 Duration of Remediation

The chloroethene mass flux and discharge values did not increase significantly over the demonstration, and, as a result, a substantial reduction in the remedial duration would not be anticipated.

7.2.6 Factors Affecting Performance

- The location and amount of biomass delivered/generated in the test plot was not directly assessed; however, a small increase in biomass density was observed in the laboratory microcosm studies. The addition of electron donor resulted in a decrease in overall microbial diversity towards those organisms that could take advantage of the electron donor supplied to the test plot. Methanogenic bacteria were not observed following biostimulation and bioaugmentation, although methane production was observed to some extent in the PTA and in the bioagumentation microcosms. The population of *Dhc* did increase, as evidenced by targeted PCR assays.

- The location and amount of electron donor injected into the test plot was evaluated through measurement of VFAs, which increased at all four center line monitoring wells during biostimulation and bioaugmentation. In addition, sulfate concentrations dropped substantially across the test plot, confirming that sufficient donor had been delivered to reduce this species.

- Geologic heterogeneity was evaluated based on hydraulic characterization of the injection wells and tracer testing conducted prior to the biostimulation phase. Overall, the tests suggested low geologic heterogeneity. Biofouling during the demonstration would have reduced the permeability of specific areas, increasing the heterogeneity in the test plot.

- Post-oxidation geochemical conditions were a factor. Geochemical conditions in the test plot prior to implementing the demonstration were mildly anaerobic (32 to -40 mV) and slightly alkaline (8.1 to 9.2), characteristic of Mn-reducing conditions; however, during biostimulation/bioaugmentation phases, both pH (7.4 to 7.6) and ORP (-265 to -295) decreased in the test plot, characteristic of sulfate-reducing or methanogenic conditions. Microcosm studies indicated that where soil samples had substantial (i.e., visibly dark) manganese dioxide, reductive dechlorination was inhibited, which is consistent with geochemical modelling results that suggest that manganese reduction may inhibit dechlorination by maintaining the hydrogen concentration below the minimum threshold required to support reductive dechlorination of cDCE and VC. Complete dechlorination to ethene was observed in bioaugmention microcosms with less manganese dioxide staining.

7.2.7 Implementation Issues

The equipment used to execute the demonstration required only minimal maintenance, with the exception of biofouling control measures. Biofouling of the injection wells impacted the implementation of the demonstration and resulted in downtime during operations; however, the biofouling control knowledge gained during this demonstration could be applied to other ISB recirculation projects. Specifically, the use of regular biofouling control agents would reduce in-line and in-well biofouling issues, and the elimination of storage tank(s) from the process equipment would help to limit opportunities for undesired biogrowth. The demonstration downtime was also negatively impacted by hurricanes and ultimately resulted in the early termination of the demonstration.

7.2.8 Mobility of the Groundwater Plume

This could not be assessed during this demonstration due to the size of the PTA relative to the size of the groundwater plume at LC34.

7.2.9 Achieve Appropriate Geochemical Conditions

During biostimulation/bioaugmentation phases, both pH (7.4 to 7.6) and ORP (-265 to -295) decreased in the test plot, characteristic of sulfate-reducing or methanogenic conditions, confirming that the appropriate geochemical conditions to promote ISB were achieved. In addition to the decreases in ORP measurements to levels characteristic of sulfate-reducing/methanogenic activity, there was strong evidence of anaerobic microbial processes usually associated with reductive dechlorination, including fermentation, manganese reduction, and sulfate reduction.

8.0 COST ASSESSMENT

8.1 COST MODEL

Costs were tracked by project milestones that were defined at the start of the demonstration in the on-line ESTCP project financial tracking system. The distribution of project funds by milestone is shown in Figure 9. The highest cost milestone was the operation of the demonstration system (including monitoring), which made up 30% of the total project cost.

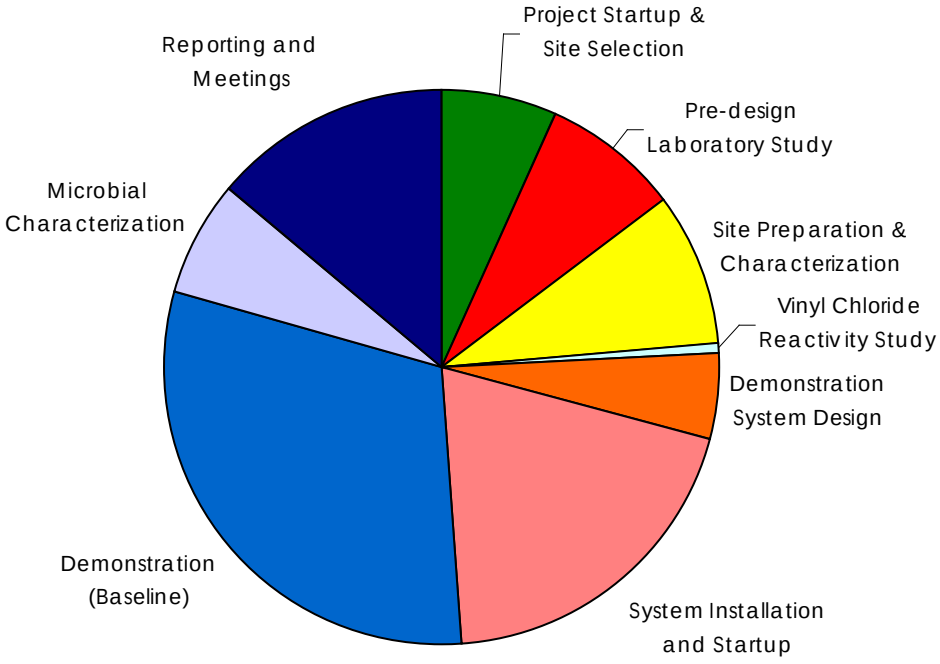


Figure 9. Distribution of project expenditures by major milestone.

The total cost of the demonstration was $843,000, resulting in the treatment of 12,500 ft^3 of soil containing approximately 370 kg of TCE. The corresponding unit costs of the demonstration are $2381/$m^3$ and $2280/kg-TCE. The unit costs incurred during the demonstration are much higher than those likely to be experienced during full-scale implement due to (1) the small scale of the demonstration, (2) the extensive monitoring effort, and (3) the implementation of a groundwater recirculation system.

Cost elements from the demonstration as they relate to potential full-scale demonstrations of a sequential ISCO-ISB remedy are presented in Table 6. Additional details of cost elements for the technology are provided in the ER-0116 Final Report, Section 5, Alternative 4, Table 5-5.

Table 6. Cost model for sequential ISCO-ISB.

Task	Notes	Cost
Site preparation & characterization	Review of site data, soil and groundwater sampling and analysis, hydraulic testing, data compilation and interpretation	$76,393
Demonstration system design	Includes preparation and submission of an Advance Data Package plus 90% and Final Work Plans for regulatory review and approval	$43,299
System installation and startup	System construction performed under subcontract with GeoSyntec supervision; start-up includes three tracer tests	$165,496
ISCO operation, maintenance and monitoring	NA – not completed as part of demonstration	--
EISB demonstration operation, maintenance and monitoring microbial characterization	Includes baseline, biostimulation, and bioaugmentation demonstration phases	$256,848
Microbial characterization	Repeated effort completed at the end of each demonstration phase	$57,330
Reporting and meetings	NA – reporting would be site-specific	--
Waste disposal	NA – not completed as part of demonstration, standard disposal	--
Long term monitoring	NA – not completed as part of demonstration, would include standard monitoring program	--
	Project Total	**$599,366**

8.2 COST DRIVERS

The principal cost drivers for the sequential technology include the costs of:

- Infrastructure, including injection well drilling and installation, aboveground piping, and process instrumentation
- O&M, including potassium permanganate injection, electron donor injection, labor required for the annual injection events, performance monitoring, and reporting.

It should be noted, as above, that the unit costs of the demonstration were high as compared to that anticipated for a typical site and that costs for alternative ISCO and ISB approaches may differ from those presented below. For example, use of batch injection approaches for both technologies may result in lower infrastructure costs as compared to recirculation approaches but provide less hydraulic control. The selection of oxidant and electron donor will also impact costs.

Manganese dioxide deposited during ISCO using potassium permanganate significantly contributes to the project cost by increasing the initial electron donor dosing requirements for ISB conducted in the ISCO treatment area. In Alternative 4 of Section 8.3, Mn-reduction, which was optimistically assumed to require only a stoichiometric electron donor dose to complete, exerted 77% of the electron donor demand. To some extent, this issue is specific to

permanganate since it is the only oxidant that results in the formation of a precipitate. However, the application of either persulfate or Fenton's reagent may also have an adverse impact on the subsequent application of ISB. The decomposition of persulfate results in the formation of sulfate, which would be present at very high concentration and, although it is a soluble species and is more likely to attenuate over time in a source area through natural groundwater flow, could exert a significant electron donor demand and competitively inhibit reductive dechlorination. Similarly, the decomposition of peroxide in Fenton's reagent results in the formation of oxygen. At high peroxide concentration, there is the potential for exsolution of oxygen gas. Trapped oxygen gas within the formation could act as a long-term source of dissolved oxygen, which is toxic to some dechlorinating microorganisms (e.g., *Dhc*).

8.3 COST ANALYSIS

8.3.1 Cost Comparison

The cost of full-scale source remediation was assessed by comparing the lifetime costs of sequential ISCO/ISB to the following technologies for a theoretical site:

- *Pump-and-treat*. Contain groundwater in the source area using groundwater extraction wells and ex situ VOC treatment;
- *ISCO*. Remove VOC mass from the source area using the injection of a concentrated solution of permanganate followed by monitored natural attenuation (MNA); and
- *ISB.* Contain groundwater in the source area and/or remove VOC mass using rapid biodegradation (ISB).

8.3.2 Cost Basis

Costing parameters are based on a theoretical site with dimensions of 100-ft long by 100-ft wide. The corresponding source area is assumed to contain 1,500,000 gallons of TCE-impacted groundwater, with the TCE source zone present from 10 to 80 ft bgs. The geology in the source area includes a sand unit from 10 to 40 ft bgs, and a silty sand unit from 40 to 80 ft bgs. The corresponding mass of impacted soil is 35.7×10^6 kg (porosity 0.3, bulk density 1800 kg/m^3). The total mass of TCE (dissolved, sorbed, and non-aqueous phase liquid [NAPL]) in the source area is 12,500 pounds, and the average groundwater concentration exiting the source area is 175 mg/L. Additional details used in the cost assessment are provided in Table 5-1 of the ER-0116 Final Report.

Capital and operating costs focus on those costs associated with the implementation of the technology and do not include costs that may be site-specific and/or equal between technologies such as regulatory approvals. The operating period of each technology was evaluated by considering the time for the source zone to be removed via dissolution using the numerical solutions proposed by Falta et al. (Falta et al., 2005a and 2005b). The use of this approach for evaluating the operating period is further described in Section 5.2.4 in the ER-0116 Final Report. All technologies were compared using the operating periods predicted based upon Falta's method at a real discount rate of 2.8% (Office of Management and Budget, 1992). A summary

of the basis of the costs for each alternative is provided in Table 5-1 of the ER-0116 Final Report. A brief description of the approach for each alternative is provided in the following sections. A summary of the costs for each alternative is provided in Table 7. Tables summarizing the cost data for each alternative are provided in Section 5 of the Final Report.

8.3.2.1 Alternative 1: Pump-and-Treat

Two groundwater extraction wells screened in either the 10-40 ft bgs or the 40-80 ft bgs depth intervals (one shallow and one deep well) and equipped with electrically operated submersible pumps. The total groundwater extraction rate is assumed to be ~5 gpm. Extracted groundwater will be treated using an air stripping tower and then recharged into the shallow aquifer via an infiltration gallery. The vapor stream from the air stripping tower will be treated using two granular activated carbon vessels connected in series. The duration of the pump-and-treat remedy to achieve a remedial goal of 5 µg/L is estimated to be 34 years using the approach described in Section 5.2.4 in the Final Report.

8.3.2.2 Alternative 2: Enhanced In Situ Bioremediation

Shallow and deep permanent injection wells (35 total) will be installed in a grid across the source area. A solution of emulsified vegetable oil (EVO) will injected through these wells with the mass of EVO based on exceeding the electron donor demand (sulfate and TCE) by a factor of four in the first year of operation. Following the first year, the source area will be amended with EVO on an annual basis with a four-fold reduction in the mass of electron donor (1X stoichiometric excess). The frequency of EVO addition would be reduced at Year 11 to once every 3 years and at Year 21 to once every 5 years. The duration of the ISB source area treatment to achieve a remedial goal of 5 µg/L is estimated to be 55 years using the approach described in Section 5.2.4 in the Final Report. However, it should be noted that substantial mass and concentration reductions may be observed in a shorter time span; for example, an ISB study at LC-34 achieved significant mass and concentration reductions within two years (Hood et al, 2008).

8.3.2.3 Alternative 3: In Situ Chemical Oxidation and Monitored Natural Attenuation

Six groundwater extraction wells and six injection wells were screened in either the 10-40 ft bgs or the 40-80 ft bgs depth intervals (three shallow and three deep wells for each line of wells) and equipped with electrically operated submersible pumps. The total groundwater extraction rate is assumed to be ~5 gpm. In the first 2 years of operation, potassium permanganate will be recirculated through the source area. The total mass of permanganate, which is based on providing sufficient oxidant to meet the demand exerted by both uncontaminated soil (1.7 g $KMnO_4$/kg soil) (IT, 2000) and TCE (2.4 mg $KMnO_4$/mg TCE), is 74,000 kg. The duration of the ISCO source area treatment to achieve a remedial goal of 5 µg/L is estimated to be 1.5 years using the approach described in Section 5.2.4 in the Final Report. However, rebound post-ISCO is commonly observed at ISCO sites, with the cost efficiency of repeating oxidant injection decreasing with each injection event. For the purposes of this cost assessment, it is assumed that ISCO results in removal of 85% of the TCE mass over the 2 years of operation. It would take an estimated additional 37 years following ISCO to meet remedial criteria of 5 µg/L through natural

attenuation processes. The O&M costs during MNA would include long-term groundwater monitoring and reporting.

8.3.2.4 Alternative 4: In Situ Chemical Oxidation and Enhanced In Situ Bioremediation

Six groundwater extraction wells and six injection wells screened in either the 10-40 ft bgs or the 40-80 ft bgs depth intervals (three shallow and three deep wells for each line of wells) and equipped with electrically-operated submersible pumps. The total groundwater extraction rate is assumed to be ~5 gpm. In the first two years of operation, potassium permanganate will be recirculated through the source area. The total mass of permanganate, which is based upon providing sufficient permanganate to meet 100% of the demand exerted by both uncontaminated soil (1.7 g $KMnO_4$/kg soil; IT, 2000) and TCE (2.4 mg $KMnO_4$/mg TCE), is 74,000 kg. It is assumed that ISCO results in removal of 85% of the TCE mass over the two years of operation (i.e., lowers the electron donor demand of TCE by 85% during ISB). Given the shorter duration of the sequential approach (and correspondingly lower number of reinjection events), EVO injections would be completed using direct push wells in this alternative. In the third year of operation, shallow and deep injection wells (20 total) will be installed in a grid across the source area. A solution of EVO will be injected through these wells with the mass of EVO based on electron donor demand of:

- Sulfate with a four-fold stoichiometric excess
- The remaining TCE (i.e., 15% of the initial TCE) with a four-fold stoichiometric excess
- Manganese dioxide (corresponding to the mass of permanganate injected in the previous 2 years) at the stoichiometric demand.

The contribution of these electron acceptors (i.e., sulfate, TCE, and manganese dioxide) to the total electron donor demand is shown in Figure 5-2 of the ER-0116 Final Report. Note that manganese dioxide exerted 77% of the total electron donor demand. In subsequent years, the source area will be amended with EVO every other year; however, the amount of electron donor required for sulfate and TCE reduction will be reduced by a factor of four, and it is assumed that manganese dioxide will not exert a further demand.

8.3.3 Life-Cycle Costs

Summaries of the costs of all four alternatives (including both capital and annual operations and maintenance) are provided in Table 7 and ER-0116 Final Report Tables 5-3, 5-4, 5-5, 5-6, and 5-7. The estimated life-cycle cost for the sequential ISCO/ISB technology is based on the capital cost of the infrastructure, plus operations and maintenance (including reagents, performance monitoring and reporting) over the period of technology implementation. Total life-cycle costs of each alternative were calculated as the net present value over the estimated operating period at a real discount rate of 2.8% (Office of Management and Budget, 1992).

The operating period of each technology was evaluated by considering the time for the source zone to be removed via dissolution using the numerical solutions proposed by Falta et al. (2005a

and 2005b). This approach uses the following variables to evaluate source zone depletion and lifespan:

- Initial source mass
- Groundwater flux through the source area
- Mass discharge rate of the chemical
- Target discharge rate of the chemical
- Mass flux enhancement factor achieved by the technology
- The relationship between remaining source mass and the contaminant mass discharge rate (what Falta et al. denote as Γ)
- Fraction of the source remaining following the initial technology (i.e., ISCO).

The values used for each of these variables are presented in Table 7. The first four variables are based upon the physical and chemical properties assumed for the theoretical site (ER-0116 Final Report Table 5-1). The mass flux enhancement factor for each technology was assumed based upon values reported in literature for field and laboratory trials of the technology. For ISB, a mass flux enhancement factor of five was considered, based on a survey of ISB laboratory and field trials by Christ et al. (2005). In addition, a second ISB scenario with a mass flux enhancement factor of 10, was considered to evaluate the sensitivity of the technology cost to that factor. For ISCO, a mass flux enhancement factor of 30 was considered, based on a survey of ISCO demonstration results performed by Krembs (2008). No mass flux enhancement (i.e., a value of 1) was used for pump-and-treat or natural attenuation. The relationship between remaining source mass and contaminant mass discharge rate, Γ, has been assumed to be 1 for the values presented in Table 7.

The predicted operating periods and total costs for each technology are summarized in Table 7. Based on this assessment, the P&T remedy would be expected to have an operating period of 34 years, ISB 55 years, ISCO/MNA 40 years, and ISCO/ISB 10 years. Without any remedial actions, the source would take an estimated 145 years to be removed through natural attenuation processes. Should the mass flux enhancement of ISB be as high as a factor of 10, there is a predicted decrease in the operating period to 29 years. Clearly, for a site where schedule is the strongest driver for technology selection ISCO/ISB has a strong advantage over all other technologies.

Final Report Table 5-3 presents a sensitivity analysis of the operating periods for Alternatives 1 and 4 to the relationship between remaining source mass and contaminant mass discharge rate (Γ). It can be seen that for the theoretical site considered, the predicted operating periods do not change substantially with changes in Γ.

In terms of capital costs (infrastructure only), ISB has the lowest capital costs. Pump-and-treat also has relatively low capital costs, primarily due to the low flow rate required to contain groundwater in the source area (5 gpm). The ISCO and ISCO/ISB options have the highest capital costs. Long-term annual O&M costs vary by alternative. ISCO is assumed to have low long-term O&M costs associated with MNA following active ISCO application. The O&M costs

for Alternatives 2 and 4, which include bioremediation, are higher since they include annual on-going electron donor addition with an aggressive dosing strategy intended to remove contaminant mass.

Overall, Alternative 2 (ISB) offers the smallest life-cycle costs, and the costs of implementing the sequential technology (Alternative 4 [ISCO/ISB]) are somewhat lower than that of implementing ISCO alone. However, the duration of the remedy is also a critical factor for most sites, and Alternative 4 clearly offers advantages as compared to all other alternatives evaluated.

The cost analysis suggests that all three aggressive in situ alternatives have lower lifetime costs than pump-and-treat, providing that they have short operating durations, as predicted in the analysis presented herein. While the ISCO/ISB option has a higher life-cycle cost than ISB alone, the shorter lifetime of sequential approach may make it more advantageous than ISB alone.

Table 7. Summary of mass flux parameters and total remedy costs for each alternative.

Technology	Source Mass (kg)	Groundwater Flux through Source (m^3/year)	Initial Discharge Rate[b] (kg/year)	Target Discharge Rate[c] (kg/year)	Mass Flux Enhancement Factor	Γ	Remaining Fraction Source Mass for Secondary Technology	Remedy Duration (years)	Total Cost of Remedy ($)
Natural attenuation	5600	1422	249	0.01	1	1	na	235	na
Source area pump-and-treat, 5 gpm	5600	9948	1741	0.05	1	1	na	34	$3,268,491
Source area bioremediation, passive approach	5600	1422	249	0.01	5	1	na	55	$1,737,483
Source area bioremediation, passive approach	5600	1422	249	0.01	10	1	na	29	$1,393,532
Source area ISCO recirculation, 85% removal / followed by MNA	5600	9948 / 1422[a]	1741 / 249	0.05 / 0.01	30 / 1	1	0.15	40	$2,801,206
Source area ISCO recirculation, 85% removal / followed by source area bioremediation	5600	9948 / 1422	1741 / 249	0.05 / 0.01	30 / 5	1	0.15	10	$2,613,724

Notes:
na – not applicable
[a]Where two values are shown, the first value represents the primary technology, the second value the secondary technology.
[b]Based on Current Conditions, TCE 175 mg/L
[c]Based on TCE MCL, 5 μg/L

9.0 IMPLEMENTATION ISSUES

The report complies with all applicable federal, state, and/or local laws and regulations. Regulations expected to affect this demonstration are listed below:

- Occupational Safety and Health Administration (OSHA) regulations
- State, local, or Cape Canaveral Air Force Base (CCAFB) regulations for underground injection of the microbial cultures, electron donors, and nutrients, and the reinjection of groundwater containing TCE and chlorinated TCE biodegradation products.

9.1 ENVIRONMENTAL CHECKLIST

9.1.1 Regulatory Issues

This section describes all applicable or relevant regulatory requirements related to the demonstration. These requirements include the acquisition of permits and the compliance with regulations. The necessary permitting and compliance issues are described below.

- *Approval from Local and State Authorities to Release Microbial Consortium.* CAFB assisted in obtaining the necessary approvals for the release of a natural consortium of microorganisms into the PTA.
- *Approval for the purchase and use of tax-free ethanol.* Geosyntec submitted a permit application from the U.S. Bureau of Alcohol, Tobacco and Firearms for the use of denatured ethanol as an electron donor for the biostimulation and bioaugmentation phases of the demonstration.

9.1.2 Hazardous Material Storage

During the demonstration, hazardous materials were stored on site in a secure location. All materials were properly stored and labeled with the appropriate labeling and placards as required by RCRA, Department of Transportation (DOT), and CCAFB. A material safety data sheet (MSDS) for each hazardous compound was kept on site in a location readily accessible to all on-site personnel.

9.1.3 Air Discharge

There were no wastes discharged to the atmosphere.

9.1.4 Wastewater Discharge

No activities planned for this demonstration generated hazardous wastewater. Groundwater extracted from the PTA was treated to remove VOCs and then reinjected into the injection wells. Purge water from sampling events were treated on site.

9.1.5 Waste Storage, Treatment, and Disposal

Soil cuttings generated during drilling activities were disposed of according to the CCAFB permit specifications. Groundwater samples submitted to off-site laboratories for analysis were managed according to the laboratory's established disposal protocols.

9.2 OTHER REGULATORY ISSUES

Results of this effort will be ensured through:

- Effective coordination with technology transfer organizations, including Federal Laboratory Consortium and National Tech Transfer Center
- Training seminars currently offered through the Remediation Technologies Development Forum
- Close coordination with the ITRC (Interstate Technology and Regulatory Council) Work Group for communication to the environmental industry and to insure rapid acceptance by industry and local governments
- Presentations at conferences and workshops.

9.3 END-USER ISSUES

Sequential application of ISCO and ISB is potentially widely applicable at chlorinated solvent sites throughout North America. However, several issues may potentially limit the widespread application of this technology. In the long term, ISCO application is likely to increase the concentration of manganese in groundwater. The capital cost associated with implementing two source control technologies (ISCO and ISB) may be a barrier to implementation. However, implementing these technologies sequentially may provide substantial schedule advantages over the implementation of either technology alone, offsetting the increased capital costs with reduced O&M costs. The uncertainty surrounding the performance of this technology is another barrier. The completion of this demonstration and publication of the results in both peer-reviewed and other technical literature will provide site managers with an improved degree of certainty when assessing either the sequential technology or ISB as a stand-alone technology.

10.0 REFERENCES

AFCEE, NFESC, and ESTCP. 2004. Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents. Prepared by Parsons Corp. Denver, CO, September 2004.

Azadpour-Keeley, A., L.A. Wood, T.R. Lee, and S.C. Mravik. 2004. Microbial responses to in situ chemical oxidation, six-phase heating, and steam injection remediation technologies in groundwater. Remediation, Autumn, 2004.

Battelle. 1999. Draft Hydrogeologic and Chemical Compilation, Interagency DNAPL Consortium Remediation Demonstration Project, Launch Complex 34, Cape Canaveral Air Station, Florida. Prepared for Interagency DNAPL Consortium.

Battelle. 2001a. Chemical Oxidation of a DNAPL Source Zone at Launch Complex 34 in Cape Canaveral Air Station, Draft Final Technology Evaluation Report. Prepared for the Interagency DNAPL Consortium, June 2001.

Battelle, 2001b. Seventh Interim Report on the IDC Demonstration at Launch Complex 34. Cape Canaveral Air Station. August, 2001.

Battelle. 2004a. Demonstration of In Situ Dehalogenation of DNAPL through Injection of Emulsified Zero-Valent Iron at Launch Complex 34 in Cape Canaveral Air Force Station, Florida (Final Innovative Technology Evaluation Report). Report prepared for the U.S. Environmental Protection Agency (USEPA), National Risk Management Research Laboratory, Superfund Innovative Technology Evaluation Program, 10 September 2004.

Battelle. 2004b. Demonstration of Biodegradation of Dense Nonaqueous-Phase Liquids (DNAPL) through Biostimulation and Bioaugmentation at Launch Complex 34 in Cape Canaveral Air Force Station, Florida (Final Innovative Technology Evaluation Report). Report prepared for the U.S. Environmental Protection Agency (USEPA), National Risk Management Research Laboratory, Superfund Innovative Technology Evaluation Program, 30 September 2004.

Christ, J.A., C.A. Ramsberg, L.M. Abriola, K.D. Pennell, and F.E. Loffler. 2005. Coupling Aggressive Mass Removal with Microbial Reductive Dechlorination for Remediation of DNAPL Source Zones: A Review and Assessment, Environmental Health Perspectives. 113(4): 465-477.

Cope, N., and J.B. Hughes. 2001. Biologically-enhanced removal of PCE from NAPL source zones, Environmental Science and Technology, 35: 2014-2021.

CRA, 1999. RCRA facility investigation report for launch complex 34 (SWMU CCAS-54) at Cape Canaveral Air Force Station, FL. Unpublished report prepared for NASA's Kennedy Space Center by CRA Services, Titusville, FL.

DiStefano, T.D., J.M. Gossett, and S.H. Zinder. 1991. Reductive dechlorination of high concentrations of tetrachloroethene to ethene by an anaerobic enrichment culture in the absence of methanogenesis. Applied and Environmental Microbiology, 57(8):2287-2292.

Duhamel, M., S.D. Wehr, L. Yu, H. Rizvi, D. Seepersad, S. Dworatzek, E.E. Cox, and E.A. Edwards. 2002. Comparison of anaerobic dechlorinating enrichment cultures maintained on tetrachloroethene, trichloroethene, cis-dichloroethene and vinyl chloride, Water Resources, 36:4193-4202, 2002.

Eddy-Dilek, C.A., B.D. Riha, D. Jackson, J. Rossabi, and J. Consort. 1998. DNAPL source zone characterization of Launch Complex 34, Cape Canaveral Air Force Station, Florida. Westinghouse Savannah River Company Report, WSRC-TR-99-00024.

Ellis, D.E., E. Lutz, J.M. Odom, R. J. Buchanan, C.J. Bartlett, M. D. Lee, M. R. Harkness, and K. A. DeWeerd. 2000. Bioaugmentation for accelerated in situ anaerobic bioremediation. Environmental Science and Technology, 34(11):224-2260.

Environmental Security Technology Certification Program [ESTCP], 1999.

Falta, R.L., P. S. Rao, and N. Basu. 2005a. Assessing the impacts of partial mass depletion in DNAPL source zones: I. Analytical modeling of source strength functions and plume response. Journal of Contaminant Hydrology, 78: 259-280.

Falta, R.L., P. S. Rao, and N. Basu. 2005b. Assessing the impacts of partial mass depletion in DNAPL source zones: II. Coupling source strength functions to plume evolution. Journal of Contaminant Hydrology, 79: 45-66.

Freeze A.R., and J.A. Cherry. 1979. Groundwater. Prentice Hall, Inc., Englewood Cliffs, New Jersey: 604p.

G&E Engineering, Inc., 1996. RCRA RFI Work for Launch Complex 34, Cape Canaveral Air Station, Breverd County, Florida. <x-apple-data-detectors://2> Prepared for NASA Environmental Program Office.

Harkness, M. R., A. A. Bracco, M.J. Brennan Jr., K.A. De Weeerd, and J. L. Spivack. 1999. Use of Bioaugmentation to Stimulate Complete Reductive Dechlorination of Trichloroethene in Dover Soil Columns. Environmental Science and Technology, 33(7): 1100-1109.

Hood, E.D., and N.R. Thomson. 2000. Numerical simulation of in situ chemical oxidation, in the proceedings of the Second International Battelle Conference on Remediation of Recalcitrant Chlorinated Compounds, Monterey, CA, May 22-25, 2000.

Hood, E.D., D.W. Major, J. Quinn, S. Yoon, A. Gavaskar, and E.A. Edwards. 2008. Demonstration of Enhanced Bioremediation in a TCE Source Area at Cape Canaveral Air Force Station, Launch Complex 34. Groundwater Monitoring and Remediation, 28(2): 98-107.

IT Corporation, 2000. In Situ Oxidation System Demonstration Test Final Report Treatment Cell C Launch Complex 34 DNAPL Source Zone Oxidation Project Cape Canaveral, FL. <x-apple-data-detectors://3>Prepared for Stephen B. Antonioli. October, 2000.

Johnson, R.L., and J.F. Pankow. 1992. Dissolution of dense chlorinated solvents into groundwater. 2. Source functions for pools of solvent. Environmental Science and Technology, 26(5):896-901.

Klens, J., D. Pohlmann, and D. Graves. 2001. The effects of permanganate oxidation on subsurface microbial populations, in the proceedings of the *Sixth International In Situ and On-Site Bioremediation Symposium*, San Diego, CA, June 4-7, 2001.

Krembs, F.J., 2008. Critical Analysis of the Field-Scale Application of In Situ Chemical Oxidation for the Remediation of Contaminated Groundwater.

Macbeth, T.W., L.N. Peterson, R.C. Starr, K.S. Sorenson Jr., R. Goehlert, K.S. Moor. In press. ISCO impacts on indigenous microbes in a PCE-DNAPL contaminated aquifer. In the proceedings of the *Eighth International Symposium of In-Situ and On-Site Bioremediation*, Baltimore, Maryland, June 6-9, 2005.

Major, D.W., M.M. McMaster, E.E. Cox, E.A. Edwards, S.M. Dworatzek, E.R. Hendrickson, M.G. Starr, J.A. Payne, and L.W. Buonamici, 2002. Field demonstration of successful bioaugmentation to achieve dechlorination of tetrachloroethene to ethene. Environmental Science and Technology, 36(23):5106-5116.

Maymo-Gatell, X., J.M. Gossett, and S.H. Zinder. 1997. *Dehalococcoides ethenogenes* Strain 195: ethene production from halogenated aliphatics. In: In Situ and On-Site Bioremediation: Volume 3. B.C. Alleman, and A. Leeson. (Eds). Battelle Press, Columbus, OH.

National Research Council. 1994. *Alternatives for ground water cleanup*. National Academy Press, Washington DC.

Office of Management and Budget. 1992. "Circular No. A-94 Revised," [Online document], 1992 October 29, [cited 2008 June], Available HTTP: http://www.whitehouse.gov/omb/circulars/a094/a094.html.

Pankow, J.F. and J.A. Cherry. 1996. Dense chlorinated solvents and other DNAPLs in Groundwater. Waterloo Press.

Rowland, M.A., and G.R. Brubaker. 2001. Effects of potassium permanganate oxidation on subsurface microbial activity. In: Proceedings of the *Sixth International In Situ and On-Site Bioremediation Symposium*, San Diego, CA, June 4-7.

Schnarr, M.J., C.L Truax, G.J. Farquhar, E.D. Hood, T. Gonullu, and B. Stickney. 1998. Laboratory and field experiments using potassium permanganate to remediate

trichloroethylene and perchloroethylene DNAPLs in porous media. Journal of Contaminant Hydrology, 29(3):205-225.

Stumm, W., and J.J. Morgan. 1970. *Aquatic Chemistry*. New York: Wiley-Interscience.

Thomson, N.R., E.D Hood, and L.K. MacKinnon. 2000. Source zone mass removal using permanganate: expectations and potential limitations, in the proceedings of *the Second International Battelle Conference on Remediation of Recalcitrant Chlorinated Compounds*, Monterey, CA, May 22-25.

U.S. Environmental Protection Agency (USEPA). 1992. Evaluation of Ground-water Extraction Remedies: Phase II, Volume 1 – Summary Report. Publication No. 9355.4-05, Office of Emergency and Remedial Response, Washington, DC.

USEPA. 1996. Drinking Water Regulations and Health Advisories. EPA/822-3-96-002. Office of Water, Washington, D.C., October.

Wiedemeier, T.H., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1999. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. U.S. Air Force Center for Environmental Excellence, v. 1&2, A324248, A324247a, A324247b.

APPENDIX A
POINTS OF CONTACT

Point of Contact	Organization	Phone Fax E-Mail	Role
Mike Deliz	Environmental Program Office NASA/ JJ-D Kennedy Space Center, FL 32899	Phone: (321) 867-6971 Fax: (321) 867-8040 E-Mail: DelizMJ@ksc.nasa.gov	Remedial Project Manager
Dave Major	GeoSyntec Consultants 130 Research Lane, Suite 2 Guelph, Ontario, Canada N1G 5G3	Phone: (519) 822-2230, Ext. 232 Fax (519) 822-3151 E-Mail: dmajor@geosyntec.com	Project Director/ Principal
Eric Hood	GeoSyntec Consultants 130 Research Lane, Suite 2 Guelph, Ontario, Canada N1G 5G3	Phone: (519) 822-2230, Ext. 225 Fax (519) 822-3151 E-Mail: ehood@geosyntec.com	Technical Lead
Leah MacKinnon	GeoSyntec Consultants 130 Research Lane, Suite 2 Guelph, Ontario, Canada N1G 5G3	Phone: (519) 822-2230, Ext. 246 Fax (519) 822-3151 E-Mail: LmacKinnon@geosyntec.com	Field Study Leader
Brent Sleep	University of Toronto Department of Civil Engineering 35 St. George Street Toronto, Ontario, Canada M5S 1A4	Phone: (416) 978-3005 Fax (416) 978-3674 E-Mail: sleep@enviro.civ.utoronto.ca	Associate Professor
Lance Hansen	Chief, Environmental Risk Assessment Branch Environmental Laboratory U.S. Army Engineer Research and Development Center 13909 Halls Ferry Road Vicksburg, MS, 39180	Phone: (601) 634-3750 Fax (601) 634-3120 E-Mail: Lance.D.Hansen@erdc.usace.army.mil	Contracting Officer's Representative (COR)
Andrea Leeson, Ph.D.	ESTCP Office 901 N. Stuart Street, Suite 303 Arlington, VA 22203	Phone: (703) 696-2118 Fax: (703) 696-2114 Andrea.Leeson@osd.mil	Environmental Restoration Program Manager

ESTCP Office
901 North Stuart Street
Suite 303
Arlington, Virginia 22203

(703) 696-2117 (Phone)
(703) 696-2114 (Fax)

E-mail: estcp@estcp.org
www.estcp.org